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# A Comparison of the Selectivity of Extraction of $[\text{PtCl}_6]^{2-}$ by Mono-, Bi- and Tripodal Receptors that Address its Outer Co-ordination Sphere

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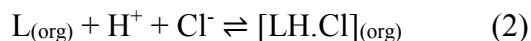
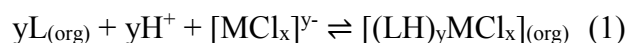
## ABSTRACT

Extraction and binding studies of  $[\text{PtCl}_6]^{2-}$  are reported for 24 mono-, bi- and tripodal extractants containing tris(2-aminoethyl)amine (TREN) or tris(3-aminopropyl)amine (TRPN) scaffolds. These reagents are designed to recognise the outer co-ordination sphere of  $[\text{PtCl}_6]^{2-}$  and to show selectivity over chloride anion under acidic conditions. Extraction from 0.6 M HCl involves protonation of the *N*-centre in tertiary amines containing one, two or three urea, amide or sulfonamide hydrogen-bond donors to set up the following equilibrium:  $2\text{L}_{(\text{org})} + 2\text{H}^+ + [\text{PtCl}_6]^{2-} \rightleftharpoons [(\text{LH})_2\text{PtCl}_6]_{(\text{org})}$ . All reagents show higher Pt-loading than trioctylamine, which was used as a positive control to represent commercial tri-alkylamine reagents. The loading of  $[\text{PtCl}_6]^{2-}$  depends on the number of pendant amides in the extractant, and follows the order tripodal > bipodal > monopodal, with urea-containing extractants outperforming amide and sulfonamide analogues. A

different series of reagents in which one, two or three of the alkyl groups in tris-2-ethylhexylamine are replaced by 3-*N'*-hexylpropanamide groups all show comparably high affinity for  $[\text{PtCl}_6]^{2-}$  and high selectivity over chloride anion in extractions from aqueous acidic solutions.  $^1\text{H}$  NMR titration of three extractants  $[\text{LH.Cl}]$  with  $[(\text{Oct}_4\text{N})_2\text{PtCl}_6]$  in  $\text{CDCl}_3$  provides evidence for high selectivity for  $[\text{PtCl}_6]^{2-}$  over chloride for tri- and di-podal extractants, which show higher binding constants than a monopodal analogue.

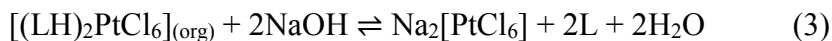
## INTRODUCTION

Solvent extraction of metals from chloride solutions underpins many processes which recover metals from the acidic chloride leaching of ores and metal wastes.<sup>1</sup> A feature of such aqueous feed streams is that the metals of value are often present as chloridometalate complexes,  $[\text{MCl}_x]^{y-}$  and consequently an effective way to transport them into a water-immiscible solvent is to form charge-neutral assemblies by transferring both protons and the chloridometalate into an extractant (L) as in equation 1. As the feed solutions usually contain a high concentration of chloride ions it is essential that the extractant shows a high selectivity for the chloridometalate over chloride to ensure that the equilibrium in equation 1 is more favourable than that in equation 2.



In order to gain an understanding of the design features which favour binding in the outer coordination spheres of chloridometalates rather than “ion pairing” to chloride, it is easier to study the extraction of kinetically inert chloridometalates such as  $[\text{PtCl}_6]^{2-}$  because they

will not exchange coordinated chloride for water or for the basic, protonatable, atom in the receptor on the time scale involved in the phase transfer reaction shown in equation 1. We have reported the use of tripodal ionophores incorporating multiple hydrogen-bond donors linked to a protonatable bridgehead nitrogen centre (**L**<sup>1</sup>-**L**<sup>5</sup>; Figure 1) to extract [PtCl<sub>6</sub>]<sup>2-</sup> into water-immiscible solvents.<sup>2-4</sup> Efficient extraction (>85%) from acidic chloride solutions was achieved with these tripodal reagents, and the quantitative stripping and release of the metalate by base (equation 3), provides the basis for a process in which the separation and concentration of platinum with recycling of the extractant and minimal reagent consumption (2 equivalents of HCl and of NaOH) and the generation of 2 mol equiv. of NaCl as a by-product.<sup>2,3</sup> Structural studies suggest that although each extractant contained three arms functionalised with potential hydrogen bond donors, only one or two of these arms participated in direct hydrogen-bond donation to the chloridometalate anion. In the majority of cases, the redundant arms in the solid state structures formed intra- and/or intermolecular hydrogen-bonds to neighbouring amide groups.<sup>2</sup> Tripodal aminoamide reagents with a different sequence of atoms linking the amide groups to the bridgehead nitrogen atom, R<sub>n</sub>N(CH<sub>2</sub>CONR'<sub>2</sub>)<sub>3-n</sub>, have been shown recently to act as efficient extractants for [RhCl<sub>5</sub>(H<sub>2</sub>O)]<sup>2-</sup> from acidic chloride solutions.<sup>5,6</sup>



We report herein the synthesis and characterisation of the novel mono- and bi-podal ionophores **L**<sup>6</sup>-**L**<sup>18</sup> (Schemes 2, 3 and 5). These retain the same hydrogen bond donor groups (urea, amide and sulfonamide), and the same solubilising alkyl and methoxy groups and a protonatable nitrogen centre that are present in the tripodal extractants **L**<sup>1</sup>-**L**<sup>5</sup> (Figure 1) but introduce mono-, bi- as well as tri-functional pendant

arms to facilitate the study of the effect of different numbers of hydrogen bond donors. The compounds **L**<sup>19</sup>-**L**<sup>24</sup> (Scheme 6) have a tertiary amine nitrogen atom carrying one, two or three 3-*N*-hexylpropanamide groups, and whilst similar to **L**<sup>1</sup>-**L**<sup>18</sup>, the sequence of the CO/NH components in the pendant amide group is reversed. These two series of extractants, **L**<sup>6</sup>-**L**<sup>18</sup> and **L**<sup>19</sup>-**L**<sup>22</sup> and **L**<sup>24</sup> have been used in experiments to extract [PtCl<sub>6</sub>]<sup>2-</sup> into chloroform to establish to what extent their strength as extractants and their selectivity over chloride ion depends on the number and type of pendant amide groups present. A comparison of PtCl<sub>6</sub><sup>2-</sup> loading by **L**<sup>24</sup> and an ether analogue in which the amine nitrogen atom has been replaced by an oxygen atom has been reported recently.<sup>7</sup>

## RESULTS AND DISCUSSION

**Synthesis and characterisation of extractants **L**<sup>6</sup> - **L**<sup>18</sup>:** The new bipodal reagents **L**<sup>6</sup> - **L**<sup>18</sup> were prepared and characterised as shown in Schemes 1 - 3 from *N,N*-bis(2-aminoethyl)-*n*-octylamine, **3** (whose synthesis has been reported previously, Scheme 1),<sup>8</sup> *N,N*-bis(3-aminopropyl)-methylamine or *N,N*-di-*n*-octyl-1,2-diaminoethane, **5**. The urea extractants **L**<sup>6</sup> and **L**<sup>7</sup> were readily obtained as white solids by reaction of **3** with two equivalents of the corresponding dimethoxyphenyl isocyanate in dry tetrahydrofuran (Scheme 2). The amido and sulfonamido analogues **L**<sup>8</sup>, **L**<sup>9</sup> and **L**<sup>10</sup> were also prepared from **3** by reaction with two equivalents of the corresponding benzoyl- or sulfonyl chloride in the presence of a base. The urea TRPN-based extractants **L**<sup>11</sup> and **L**<sup>12</sup> were obtained as white solids by reaction of *N,N*-bis(3-aminopropyl)-methylamine (Scheme 3). The amido analogue **L**<sup>13</sup> was also prepared from *N,N*-bis(3-aminopropyl)-methylamine by reaction with two equivalents of the 3,4,5-trimethoxybenzoyl chloride in the presence of a base (Scheme 3). All extractants were purified by column chromatography.

Amine **5** was prepared, in high yield, by adaptation of a literature procedure (Scheme 4),<sup>9</sup> and was converted to **L**<sup>14</sup> - **L**<sup>18</sup> (Scheme 5) using similar procedures to those described above for **L**<sup>6</sup> - **L**<sup>13</sup>. Extractants **L**<sup>14</sup> and **L**<sup>15</sup> are white solids, whereas **L**<sup>16</sup> - **L**<sup>18</sup> were obtained as yellow oils after purification by column chromatography.

**Synthesis and characterisation of extractants **L**<sup>19</sup> – **L**<sup>23</sup>:** The mono-, bi- and tripodal extractants **L**<sup>19</sup> – **L**<sup>21</sup> and **L**<sup>23</sup> were prepared (Scheme 6) by Michael addition reactions of the appropriate amine and methyl acrylate to give the esters **6** - **8** under conditions similar to those used by Surendra *et al.*,<sup>10</sup> followed by aminolysis with *n*-hexylamine (**L**<sup>19</sup> – **L**<sup>22</sup>) or *iso*-butylamine (**L**<sup>23</sup>). **L**<sup>19</sup>, **L**<sup>20</sup> and **L**<sup>23</sup> are pale yellow oils, whereas **L**<sup>21</sup> was obtained as a white solid after washing with hexane. **L**<sup>22</sup> was prepared by aminolysis of *N*-methylhexylacrylamide (**10**) and **L**<sup>24</sup> as described previously.<sup>7</sup> Extractants **L**<sup>23</sup> and **L**<sup>24</sup> have the same atom sequence linking the tertiary amine and the amide units as **L**<sup>19</sup>-**L**<sup>22</sup> but have smaller/more rigid *N*-alkyl substituents, chosen to make growing single crystals of complexes with [PtCl<sub>6</sub>]<sup>2-</sup> easier. **L**<sup>24</sup> also has a tertiary amide group and was used to test whether the absence of an amido N-H has a major deleterious effect on binding to the outer coordination sphere of [PtCl<sub>6</sub>]<sup>2-</sup>.

**Single-crystal X-ray structure of **L**<sup>11</sup>:** Crystals were grown by the vapour diffusion of Et<sub>2</sub>O into a concentrated solution of the product in MeOH and have the monoclinic space group *P*21/*c* with two independent molecules in the asymmetric unit, **L**<sup>11(a)</sup> and **L**<sup>11(b)</sup> (see Supplementary Information). In **L**<sup>11(a)</sup> the urea functionalities form intra- and intermolecular bifurcated hydrogen-bonds to give the chain shown in Figure 2. Similar

chains are formed by  $\mathbf{L}^{11(b)}$  with  $\text{N10} \cdots \text{H10A} \cdots \text{O3}$  ( $\text{H} \cdots \text{A} = 2.204 \text{ \AA}$ ) and  $\text{N9} \cdots \text{H9A} \cdots \text{O3}$  ( $\text{H} \cdots \text{A} = 2.161 \text{ \AA}$ ). More details of the hydrogen-bonding in the structure of  $\mathbf{L}^{11}$  and the crystallographic data and structure refinement details are given in Supporting Information.

**Synthesis of complexes of  $[\text{PtCl}_6]^{2-}$ :** Charge-neutral ion-pair complexes of  $[\text{PtCl}_6]^{2-}$  with monoprotonated  $\mathbf{L}^6 - \mathbf{L}^{18}$  and  $\mathbf{L}^{23}$  were formed by the reaction of  $\mathbf{L}$  with  $[\text{H}_2\text{PtCl}_6]$  in  $\text{CH}_3\text{OH}$  or  $\text{CH}_3\text{CN}$ . Elemental analysis, mass spectrometry and  $^1\text{H}$ -NMR spectroscopy of these complexes support the formation of 2:1  $(\mathbf{LH})^+ : [\text{PtCl}_6]^{2-}$  complexes.  $[(\mathbf{L}^{24}\text{H})_2\text{PtCl}_6]$  was formed by contacting a solution of  $\mathbf{L}^{24}$  in toluene with  $[\text{H}_2\text{PtCl}_6]$  in 6M aqueous HCl. The third phase was collected and crystals suitable for X-ray diffraction were grown by diffusion of diethyl ether into a methanol solution of the third phase.

#### **X-ray crystal structures of $[(\mathbf{L}^n\text{H})_2\text{PtCl}_6]$ complexes.**

X-ray structure determinations of  $[(\mathbf{L}^{11}\text{H})_2\text{PtCl}_6]$ ,  $[(\mathbf{L}^{13}\text{H})_2\text{PtCl}_6]$ ,  $[(\mathbf{L}^{23}\text{H})_2\text{PtCl}_6]$  and  $[(\mathbf{L}^{24}\text{H})_2\text{PtCl}_6]$  (Figures 3-6) confirm that the extractant is protonated at the tertiary amine nitrogen atom and that the resulting monocations  $\mathbf{LH}^+$  form neutral 2 : 1 assemblies with a  $\text{PtCl}_6^{2-}$  ion.

The strongest hydrogen bonds to the chloridoplatinate ions are formed by amide N-H groups which usually interact with more than one outer-sphere chloride atom. Thus, in  $[(\mathbf{L}^{11}\text{H})_2\text{PtCl}_6]$ , Figure 3, the amide hydrogen atom attached to N5 is located over the triangular face defined by Cl1, Cl2 and Cl3, making its closest contact with Cl2 and that attached to N4 lies close to the edge defined by Cl2 and Cl3. The centres of faces and the

edges of the octahedron correspond to areas of highest electron density surrounding  $[\text{PtCl}_6]^{2-}$  and are locations predicted to be targeted by NH groups.<sup>11-15</sup> The three shortest  $\text{NH}\cdots\text{Cl}$   $[\text{PtCl}_6]^{2-}$  contacts formed by each  $\text{L}^{11}\text{H}^+$  cation are:  $\text{N4—H4A}\cdots\text{Cl2}$  (2.604 Å),  $\text{N4—H4A}\cdots\text{Cl3}$  (2.745 Å) and  $\text{N5—H5A}\cdots\text{Cl2}$  (2.729 Å) (Figure 3).

As previously observed<sup>2</sup> with the tripodal extractants, the urea-containing reagents have a propensity to form both intra- and intermolecular hydrogen bonds to each other. This is also found to be the case for the bipodal  $\text{L}^{11}\text{H}^+$  in  $[(\text{L}^{11}\text{H})_2\text{PtCl}_6]$ . One urea group in each cation forms hydrogen-bonds to a  $[\text{PtCl}_6]^{2-}$  anion whilst the other links to a  $\text{L}^{11}\text{H}^+$  cation in an adjacent molecule to give a  $\cdots((\text{L}^{11}\text{H}^+)\cdots[\text{PtCl}_6]^{2-}\cdots(\text{L}^{11}\text{H}^+))\cdots((\text{L}^{11}\text{H}^+)\cdots[\text{PtCl}_6]^{2-}\cdots(\text{L}^{11}\text{H}^+))\cdots$  chain. The details of the hydrogen-bonds present in this structure and the other  $[(\text{LH})_2\text{PtCl}_6]$  complexes, together with the crystallographic data and structure refinement details are given in Supporting Information.

In the solid-state structure of  $[(\text{L}^{13}\text{H})_2\text{PtCl}_6]$  the two amide arms of each  $\text{L}^{13}\text{H}^+$  receptor addresses a different  $[\text{PtCl}_6]^{2-}$  anion (Figure 4) with  $\text{N2—H2A}\cdots\text{Cl2}$  ( $\text{H}\cdots\text{A} = 2.464$  Å) and  $\text{N3—H3A}\cdots\text{Cl3}$  ( $\text{H}\cdots\text{A} = 2.581$  Å), giving a chain structure. The centre of inversion at the platinum atom ensures that four amido N-H groups form hydrogen-bonds to the chloridoplatinate.

The NH unit of the protonated tertiary amine nitrogen atom in  $[(\text{L}^{23}\text{H})_2\text{PtCl}_6]$  forms a H-bond to the neighbouring amide oxygen atom to form a 6-membered “proton chelate”. The chelated proton does not form hydrogen bonds to other atoms, but the chelate ring defines the disposition of polarised N-H and C-H bonds which address the outer coordination sphere of a chloridoplatinate through  $\text{N—H}\cdots\text{Cl}$  and  $\text{C—H}\cdots\text{Cl}$



interactions. This results in a polymeric structure (Figure 5) in which each chloridoplatinate forms twelve contacts of less than 3 Å to  $\text{L}^{23}\text{H}^+$  units : two amido  $\text{N}—\text{H}\cdots\text{Cl}$  interactions,  $\text{N5A}—\text{H5A}\cdots\text{Cl4C}$  ( $\text{H5A}\cdots\text{Cl4C} = 2.637$  Å) and  $\text{N5B}—\text{H5B}\cdots\text{Cl6C}$  ( $\text{H5B}\cdots\text{Cl6C} = 2.468$  Å) and a further ten  $\text{C}—\text{H}\cdots\text{Cl}$  interactions between 2.768 and 2.903 Å  $\text{H}\cdots\text{Cl}$  length. One chloride ligand has no interactions within 3 Å, but does show six slightly longer interactions (between 3 and 3.5 Å) with neighbouring  $\text{C}—\text{H}$  groups, four of which are notably  $\text{C}—\text{H}$  groups adjacent to the protonated amine nitrogen atom.

The two crystallographically independent  $[\text{L}^{24}\text{H}]^+$  receptors in  $[(\text{L}^{24}\text{H})_2\text{PtCl}_6]$  also contain a 6-membered “proton chelate” which templates the binding sites to provide six polarised  $\text{C}—\text{H}$  bonds to interact with the  $[\text{PtCl}_6]^{2-}$  anion as shown in Figure 6. The assembly formed by  $[\text{L}^{24}\text{H}]^+$  is fundamentally different from those formed by the other receptors, having only  $\text{C}—\text{H}\cdots\text{Cl}$  interactions because it does not contain any amido  $\text{N}—\text{H}$  groups and the ammonium proton is not available as it is chelated by the amido  $\text{C}=\text{O}$  group. Interactions are predominantly short contacts between four of the  $\text{C}—\text{H}$  donor groups in the  $\alpha$ -position to two protonated amines and four of the six chloride ligands. Interactions range from 2.641 Å to 2.993 Å (see Supplementary Information). Two of these interactions are bifurcated, each of which  $\text{C}—\text{H}$  interact with opposing edges of the octahedral chloridometalate. A further four interactions with aryl  $\text{C}—\text{H}$  donors are observed which appear to be circumstantial interactions due to the steric bulk of the receptors. These steric effects also prevent interaction of any kind between the receptors and the sixth chloride ligand.

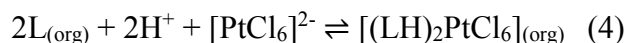
X-ray structures confirm that the extractants can form a large number of  $\text{N}—\text{H}$  and weaker  $\text{C}—\text{H}$  hydrogen bonding contacts with the outer-sphere of  $[\text{PtCl}_6]^{2-}$  consistent with

this being a “soft anion”. These soft receptors are well suited to show a preference for chloridometalate anions over the “harder” chloride ion in extraction processes. This selectivity should be complemented by the Hofmeister bias<sup>16,17</sup> which favours the extraction of the anion with the lower hydration energy,  $[\text{PtCl}_6]^{2-}$ , in this case.

**Potentiometry:** Titration of the bipodal extractants  $\text{L}^{12}$  and  $\text{L}^{13}$  in acetonitrile/water confirms that, like their tripodal analogues  $\text{L}^1$  and  $\text{L}^3$  reported previously,<sup>1</sup> these are readily protonated, and the pKa values obtained (Table 1) are consistent with protonation occurring at the tertiary amine nitrogen atom. It has been shown<sup>18,19</sup> that protonation of amino-amide receptors with similar structures to  $\text{L}^{19}$  -  $\text{L}^{24}$ , having the atom sequence  $\text{R}_2\text{NCH}_2\text{CH}_2\text{CONR}_2$ , leads to the formation of an intramolecular hydrogen bond between the ammonium  $\text{NH}^+$  group and the neighbouring carbonyl group. The formation of such six membered proton chelates by  $\text{L}^{23}$  and  $\text{L}^{24}$  is demonstrated in the solid state structures of  $[(\text{L}^{23}\text{H})_2\text{PtCl}_6]$  and  $[(\text{L}^{24}\text{H})_2\text{PtCl}_6]$  discussed above, and an eight-membered ring analogue is present in  $[(\text{L}^{11}\text{H})_2\text{PtCl}_6]$ . Consequently the differences in pKa values in Table 1 and in the effective basicities of the extractants in solvent extraction experiments are more likely to result from variations in ability to chelate the added proton than from the effect of the substituent upon the electron density on the amino nitrogen atom.

**Solvent extraction:** The relative ability of reagents  $\text{L}^6$ – $\text{L}^{22}$  and  $\text{L}^{24}$  to extract the hexachloridoplatinate from acidic chloride solutions (Equation 4) was investigated as previously reported<sup>2</sup> by determining the dependence of Pt-loading on the extractant

concentration. Results are summarized in Figures 7a – 7e and in Table 5 along with data for trioctylamine (**TOA**), which has been shown<sup>20</sup> to be an effective extractant for octahedral  $[\text{MCl}_6]^{2-}$  chloridometalates and is a model for the Alamine® reagents developed originally by General Mills.<sup>1,21</sup>



Apart from **L**<sup>11</sup> which was too insoluble in chloroform and **L**<sup>23</sup> which was too soluble in water in its protonated form to allow solvent extraction experiments to be performed, all of **L**<sup>1</sup> – **L**<sup>22</sup> show higher loadings of  $[\text{PtCl}_6]^{2-}$  than **TOA**, suggesting that the distribution coefficients for the extraction shown in equation 4 are favourably influenced by the incorporation of hydrogen bond donor groups into the trialkylammonium unit. For the TREN and TRPN-containing reagents, **L**<sup>1</sup> - **L**<sup>18</sup>, analysis of the dependence of  $[\text{PtCl}_6]^{2-}$  loading on the nature and type of amide substituent is most easily followed by the comparison of **L**<sup>1</sup>, **L**<sup>3</sup>, **L**<sup>5</sup>, **L**<sup>6</sup>, **L**<sup>8</sup>, **L**<sup>10</sup>, **L**<sup>14</sup>, **L**<sup>16</sup> and **L**<sup>18</sup> which all have 3,4-dimethoxy-substitution of the pendant phenyl group. The 3,5-dimethoxyphenyl compounds show very similar loading properties to their 3,4-isomers (see Table 2 and Supporting Information) and have thus been largely excluded from the discussion below.

The general trend in the strength as an extractant for a particular type of amide in TREN-based systems, **L**<sup>1</sup>-**L**<sup>18</sup>, varies in the order tripodal > bipodal > monopodal extractant. The efficiency of loading falls off particularly sharply for the “simple” amides, e.g. when a 3-fold excess of the reagent is present the loadings are for **L**<sup>3</sup> (tripodal) 87%, **L**<sup>8</sup> (bipodal) 30% and for **L**<sup>16</sup> (monopodal) 13% [for their 3,5-methoxy isomers **L**<sup>4</sup>, **L**<sup>9</sup> and **L**<sup>17</sup> the values vary similarly: 86, 25 and 9%].

In terms of the type of hydrogen bonding substituent present in the arms of the receptor, the incorporation of urea units leads to the strongest extractants. For both the tripodal and monopodal systems the distribution coefficients for  $[\text{PtCl}_6]^{2-}$  loading (Table 2) follow the order ureas > amides > sulfonamides. Thus for the tripodal urea, amido and sulfonamido extractants **L**<sup>1</sup>, **L**<sup>3</sup> and **L**<sup>5</sup> the recovery of Pt by chloroform solutions containing a 50% excess of extractant is 98, 87 and 77% (Figure 7a and Table 2), and for the monopodal analogues, **L**<sup>14</sup>, **L**<sup>16</sup> and **L**<sup>18</sup>, under similar conditions (Table 2) recoveries of 50, 13 and 10% were recorded. For the bipodal series **L**<sup>6</sup> (65%), **L**<sup>8</sup> (30%) and **L**<sup>10</sup> (53%) the order (Table 2) is different with the amide being the weakest extractant.

The extractant series containing the reversed CO/NH amido functionality (**L**<sup>19</sup>-**L**<sup>21</sup>) shows very different extraction properties. There is very little difference in strength between the mono-, bi- and tripodal reagents and all show complete, or very nearly complete, recovery of platinum when ca. 2 mol of reagent is used in the extraction. This implies that the extractants show very high selectivity for  $\text{PtCl}_6^{2-}$  over  $\text{Cl}^-$ , i.e. the anion exchange equilibrium  $2[(\text{LH})\text{Cl}]_{(\text{org})} + \text{PtCl}_6^{2-} \rightleftharpoons [(\text{LH})_2\text{PtCl}_6]_{(\text{org})} + 2\text{Cl}^-$ , is displaced to the right despite chloride being present in approximately an 60-fold excess over chloridoplatinate. When the monopodal reagent **L**<sup>19</sup> was modified to contain a tertiary amide unit (**L**<sup>22</sup>), markedly different strengths were observed. Greater than 6 mol of reagent was required to recover >95%  $\text{PtCl}_6^{2-}$ . A similar situation has been recorded for the extraction of  $[\text{ZnCl}_4]^{2-}$  from 6M HCl solutions by these and similar reagents.<sup>18,19</sup> In these systems the protonation of the bridgehead nitrogen atom is always accompanied by formation of a hydrogen bond to an amido oxygen, giving a six-membered “proton chelate” (Figure 8). This pre-organises the receptor to provide amido N-H hydrogen

bond donors and polarised C-H bonds to address the “soft”, charge diffuse, chloridometalate anion. Where sterically feasible the harder chloride anion interacts with *both* the amido and ammonium N-H hydrogen bond donors. The greater strength of **L**<sup>19</sup> which has a secondary amide group over **L**<sup>22</sup> which has a tertiary amide group, but otherwise a very similar structure, demonstrates the effectiveness of polarised amido N-H units as hydrogen bond donors in addressing the outer-coordination sphere of chloridometalates.

**<sup>1</sup>H NMR solution studies:** The results above indicate that the incorporation of amido hydrogen bond donor groups enhances Pt-extraction from acidic chloride solutions. It is of interest to establish whether these variations in strength of extraction are mirrored by the strength of the binding of the cationic receptors, **L**<sup>n</sup>H<sup>+</sup>, to the outer coordination sphere of PtCl<sub>6</sub><sup>2-</sup>. <sup>1</sup>H-NMR titrations were carried out in a single phase, CDCl<sub>3</sub>, to follow the change in the shifts of characteristic signals in the spectra of the receptors **L**<sup>n</sup>H<sup>+</sup> present in the form of their chloride salts when [PtCl<sub>6</sub>]<sup>2-</sup> was added in the form of its chloroform-soluble derivative, **9** [(Oct<sub>4</sub>NH)<sub>2</sub>PtCl<sub>6</sub>], in the exchange reaction shown in equation (5). The tri-, di- and monopodal amido extractants **L**<sup>4</sup>, **L**<sup>9</sup> and **L**<sup>17</sup> (Figure 9) were selected for study on the basis of the good solubilities of their hydrochloride salts and chloridoplatinate complexes in chloroform, and **TOA** was used for comparison because this contains no pendant hydrogen bond donor groups. The hydrochloride salts, **L**<sup>4</sup>•HCl, **L**<sup>9</sup>•HCl and **L**<sup>17</sup>•HCl, were synthesized by bubbling hydrogen chloride into solutions in chloroform or *n*-hexane.



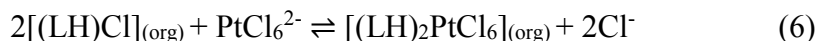
## 9

Results from the titrations are presented in Figure 9. In all cases the ammonium proton, shown in black, experiences a significant upfield shift but there is no clear pattern for the direction of the shifts for the other protons in  $\text{L}^4\text{H}^+$ ,  $\text{L}^9\text{H}^+$  and  $\text{L}^{17}\text{H}^+$ . Whilst the analysis of results is complicated by the number of species present (see below and SI, Fig SI7), the values for formation of the 2 : 1 assemblies (Table 3), evaluated using a purpose-written computer program,<sup>22</sup> are consistent with the tri- and di-amido receptors  $\text{L}^4$  and  $\text{L}^9$  ( $K_{\text{ex}}$   $6 \times 10^5$  and  $1 \times 10^5 \text{ M}^{-2}$ , respectively) being stronger extractants than the mono-amido reagent  $\text{L}^{17}$  and **TOA** which have  $K_{\text{ex}}$  values of  $4 \times 10^3$  and  $7 \times 10^3 \text{ M}^{-2}$ , respectively. These variations in the formation constants are consistent with the variation in extraction strength and suggest that the presence of stronger H-bond donor groups in a receptor enhances the complex stability in solution. However, caution needs to be exercised in coming to this conclusion because the exchange equilibrium in equation 5 is also dependent on the relative stabilities of the chloride assemblies  $\text{L}^4\text{H}\cdot\text{Cl}$  and  $\text{Oct}_4\text{N}\cdot\text{Cl}$ . It is probable, based on the structures of the complexes in the solid state and on computational modelling of the interactions of similar receptors with  $\text{ZnCl}_4^{2-}$  or  $\text{PtCl}_6^{2-}$  that inter- and intra-molecular hydrogen bonding between amido groups occurs, particularly at high concentration of receptor relative to metalate.<sup>7,19</sup> These may need to be broken to adopt the optimum conformation to bind to the  $\text{PtCl}_6^{2-}$  guest and the energies required to do this could vary considerably between the mono-, di- and tri-amido extractants. Evidence for changes to inter- or intramolecular hydrogen bonding in  $\text{L}^4\text{H}^+$  is provided by monitoring the chemical shifts of the amido NH and the adjacent aromatic

and methoxy hydrogen atoms when it is titrated with  $[(\text{Oct}_4\text{NH})_2\text{PtCl}_6]$  (see Figure SI7). These pass through maxima and minima before the stoichiometric quantity (0.5 equivalents) of  $\text{PtCl}_6^{2-}$  has been added.

## CONCLUSIONS

The efficacy of the new mono- and bipodal receptors in recovering platinum from acid chloride feed solutions has been established. For the TREN and TRPN-based extractants  $\text{L}^{1-18}$ , those containing urea groups outperform amide and sulfonamide analogues. Both the mono- and bipodal receptors fail to achieve as high platinum loadings as their tripodal analogues  $\text{L}^1\text{-L}^5$ . Whilst this indicates that the number of hydrogen-bond donor groups plays an important role in defining the efficiency of Pt-recovery, it is not clear whether this is simply a consequence of increasing the stability of the  $[(\text{LH})_2\text{PtCl}_6]$  assemblies via formation of more effective interactions between N-H groups and the outer coordination sphere of the chloridometalate anion. Under the conditions used in the extraction experiments chloride ions are present in large (ca. 30-fold) excess and selectivity of extraction over chloride is a key issue in determining Pt-loading (see equation 6). The multiplicity of H-bond donors present in receptors such as  $\text{L}^{11}$  and  $\text{L}^{13}$  could favour formation of 2:1 assemblies whose stoichiometry is supported by  $^1\text{H}$  NMR titrations with larger chloridometalate than with smaller chloride ion. However, the possible overprovision of H-bond donors in the TREN and TRPN-based receptors is suggested by crystal structures of  $[(\text{L}^{11}\text{H})_2\text{PtCl}_6]$  and  $[(\text{L}^{13}\text{H})_2\text{PtCl}_6]$  in which polymeric assemblies allow the urea and amide units to use their H-bond donors to greater effect in interacting with the chloride atoms of the  $[\text{PtCl}_6]^{2-}$  ion.



The behaviour of the receptors **L**<sup>19</sup>-**L**<sup>22</sup> which contain amide arms linked to the bridgehead amine nitrogen atom by the sequence NCH<sub>2</sub>CH<sub>2</sub>CONH is different. These all show almost complete extraction when 2 mol equivalent of the extractant are present. The very high selectivity of extraction of [PtCl<sub>6</sub>]<sup>2-</sup> over Cl<sup>-</sup> implied by these results is thought to arise from the protonation of the amine being accompanied by the formation of a 6-membered “proton chelate” ring. This prevents the ammonium N-H unit forming bonding interactions with either anion and “templates” the receptor to provide several amido N-H H-bond donors and polarised C-H bonds to address the “soft”, charge diffuse, chloridometalate anion. In this form the receptor **L**<sup>22</sup> has *only* polarised C-H bonds to interact with the chloridometalate and is shown to be a weaker extractant than those with amido N-H donor, although the extractant is still significantly stronger than TOA.

## EXPERIMENTAL SECTION

All solvents and reagents were obtained from Aldrich or Fisher. The synthesis of **L**<sup>1</sup>-**L**<sup>5</sup> and **L**<sup>24</sup> as well as their extraction results have been reported previously.<sup>1,7</sup> The amine **3** was prepared following a literature procedure<sup>8</sup> and amine **5** by adaptation of a literature procedure.<sup>9</sup> <sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained on Bruker ARX 250, DPX 360, DPX 300, DPX 400 or AVA 500 spectrometers. The chemical shifts (δ) are reported in parts per million (ppm) relative to the residual proton solvent signal in CDCl<sub>3</sub> (δ<sub>H</sub> 7.26 and δ<sub>C</sub> 77.0). Fast atom bombardment (FAB) mass spectra were recorded on a Kratos MS50TC instrument in a 3-nitrobenzyl alcohol (NOBA) matrix. Electrospray (ES) mass spectra



were recorded on a VG Autospec instrument. ICP-MS was carried out using the Thermo-Fisher Scientific X-Series<sup>II</sup>.

**General Experimental Procedure for Extractions:** Analytical grade  $\text{CHCl}_3$  was used to prepare the receptor solutions without further purification. Water used to prepare the solutions of  $[\text{H}_2\text{PtCl}_6]$  was purified using a commercial filtration system and reported to a resistance of approximately  $18\Omega$ . The acid  $[\text{H}_2\text{PtCl}_6]\cdot 6\text{H}_2\text{O}$ , which was purchased from Aldrich, was dried over  $\text{P}_2\text{O}_5$  to obtain a yellow solid. Calibration curves for ICP-OES and ICP-MS were prepared by dilution of commercially available standards.

Solutions of receptor were prepared at varying concentrations between 0.0005 and 0.01 M by weighing aliquots of a receptor stock solution (0.01 M in  $\text{CHCl}_3$ ) into 5  $\text{cm}^3$  volumetric flasks and diluting to the mark with  $\text{CHCl}_3$ . Solutions of  $[\text{H}_2\text{PtCl}_6]$  were prepared by weighing  $[\text{H}_2\text{PtCl}_6]\cdot 6\text{H}_2\text{O}$  (0.03 g) into a 50  $\text{cm}^3$  volumetric flask and diluting to the mark with 0.6 M HCl.

Extractions were prepared by charging 100  $\text{cm}^3$  Schott flasks, fitted with a magnetic stir bar, with solutions of the receptor (5  $\text{cm}^3$ ) and  $[\text{H}_2\text{PtCl}_6]$  solution (5  $\text{cm}^3$ ). The extractions were stirred at 25 °C for 4 h, after which time the phases were separated. Aqueous samples for ICP-OES analysis were prepared by transferring *ca.* 2  $\text{cm}^3$  of the aqueous phase into weighed 5  $\text{cm}^3$  volumetric flasks, weighing and diluting to the mark with water; samples for ICP-MS were diluted by a thousand fold using 0.6 M HCl as the diluent. The organic phases (4.0  $\text{cm}^3$ ) were transferred into glass snap-top vials, fitted with magnetic stir bars, using a volumetric glass pipette. An aliquot of aqueous NaOH (0.06 M) was added to these vials so that there were two molar equivalents of  $\text{OH}^-$  relative to the amount of receptor in the sample, as well as sufficient water to make the

final aqueous volume 4 cm<sup>3</sup>. The two phases were contacted for 30 min then separated. Samples for ICP-OES analysis were prepared by weighing the aqueous phase (2 cm<sup>3</sup>) into 5 cm<sup>3</sup> volumetric flasks and diluting to the mark with water. To determine the concentration of Pt in the stock solution by ICP-OES or ICP-MS analyses, samples were prepared by weighing in the same manner as the above aqueous extraction samples.

**General experimental procedure for <sup>1</sup>H NMR titrations:** A stock solution of the hydrochloride salt of the appropriate extractant (host) was prepared at a known concentration in CDCl<sub>3</sub>. Solutions of bis(tetra-*n*-octylammonium)hexachlorido platinum(IV) (**9**) were prepared at a known concentrations by dissolution in host solutions so that no dilution of the host occurred during the titration, and the <sup>1</sup>H NMR spectra were recorded on a Bruker 300 MHz spectrometer. The observed changes in chemical shift of the host signals as a function of guest concentration were analysed using purpose-written software,<sup>16</sup> which yields the association constant (*K*<sub>ex</sub>), the bound chemical shift and the free chemical shift.

*Compound L<sup>6</sup>:* Amine **3**<sup>8</sup> (0.24 mmol) was dissolved in anhydrous THF (10 cm<sup>3</sup>) under N<sub>2</sub> and a solution of 3,4-dimethoxyphenyl isocyanate (0.52 mmol) in anhydrous THF (10 cm<sup>3</sup>) was added dropwise with stirring at room temperature. The reaction was stirred at room temperature for 5 h. The solvent was removed to give a yellow oil, which was purified by column chromatography on silica gel using 97% EtOAc, 3% MeOH to afford the desired product as a white powder. Yield: 90%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.71 (br, 2H, NH), 6.94 (s, 2H, ArH), 6.63 (br, 4H, ArH), 6.35 (br, 2H, NH), 3.76 (s, 6H, OCH<sub>3</sub>), 3.71 (s, 6H, OCH<sub>3</sub>), 3.18 (br, 4H, CH<sub>2</sub>), 2.42 (br, 4H, CH<sub>2</sub>), 2.32 (t, 2H, CH<sub>2</sub>, <sup>3</sup>*J*<sub>HH</sub> = 6.6 Hz), 1.32-1.18 (m, 12H, CH<sub>2</sub>), 0.81 (t, 3H, CH<sub>3</sub>, <sup>3</sup>*J*<sub>HH</sub> = 7.3 Hz) ppm; <sup>13</sup>C

NMR: (75 MHz, CDCl<sub>3</sub>):  $\delta$  157, 149, 145, 133, 113, 111, 105, 56, 56, 55, 38, 32, 30, 30, 27, 27, 23, 14 ppm; MS (ES<sup>+</sup>): 574 [M+H]<sup>+</sup>, 596 [M+Na]<sup>+</sup>; IR (Nujol, cm<sup>-1</sup>): 3326 ( $\nu_{\text{NH}}$ ), 1645 ( $\nu_{\text{C=O}}$ ), 1509 ( $\nu_{\text{Ar}}$ ); Anal. Calcd. for C<sub>30</sub>H<sub>47</sub>N<sub>5</sub>O<sub>6</sub>: C, 62.80; H, 8.26; N, 12.21. Found: C, 62.59; H, 8.23; N, 12.13.

*Compound L<sup>7</sup>*: Amine **3**<sup>8</sup> (0.79 mmol) was dissolved in anhydrous THF (20 cm<sup>3</sup>) under N<sub>2</sub> and a solution of 3,5-dimethoxyphenyl isocyanate (1.60 mmol) in anhydrous THF (30 cm<sup>3</sup>) was added dropwise with stirring at room temperature. The reaction was stirred at room temperature for 5 h. The solvent was removed to give a yellow oil, which was purified by column chromatography on silica gel using 97% EtOAc, 3% MeOH to afford the desired product as a white powder. Yield: 84%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.32 (br, 2H, NH), 6.61 (s, 4H, ArH), 6.50 (br, 2H, NH), 6.27 (s, 2H, ArH), 3.66 (s, 12H, OCH<sub>3</sub>), 3.24 (br, 4H, CH<sub>2</sub>), 2.48 (br, 4H, CH<sub>2</sub>), 2.40 (t, 2H, CH<sub>2</sub>, <sup>3</sup>J<sub>HH</sub> = 6.2 Hz), 1.27-1.15 (m, 12H, CH<sub>2</sub>), 0.84 (t, 3H, CH<sub>3</sub>, <sup>3</sup>J<sub>HH</sub> = 6.1 Hz) ppm; <sup>13</sup>C NMR: (75 MHz, CDCl<sub>3</sub>):  $\delta$  161, 156, 143, 99, 95, 57, 55, 50, 41, 32, 31, 30, 27, 25, 23, 14 ppm; MS (ES<sup>+</sup>): 574 [M+H]<sup>+</sup>, 596 [M+Na]<sup>+</sup>; IR (Nujol, cm<sup>-1</sup>): 3332 ( $\nu_{\text{NH}}$ ), 1649 ( $\nu_{\text{C=O}}$ ); Anal. Calcd. for C<sub>30</sub>H<sub>47</sub>N<sub>5</sub>O<sub>6</sub>: C, 62.80; H, 8.26; N, 12.21. Found: C, 62.48; H, 8.29; N, 12.10.

*Compound L<sup>8</sup>*: Amine **3**<sup>8</sup> (0.23 mmol) was dissolved in water (10 cm<sup>3</sup>) containing NaOH (0.75 mmol). 3,4-Dimethoxybenzoyl chloride (0.49 mmol) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (10 cm<sup>3</sup>) and added slowly to the amine solution. The reaction was stirred at room temperature overnight. The organic layer was separated, dried with MgSO<sub>4</sub>, filtered and the solvent removed to give a yellow oil, which was purified by column chromatography on silica gel using 97% CH<sub>2</sub>Cl<sub>2</sub>, 3% MeOH to afford the desired product as a white powder. Yield: 74%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.41 (d, ArH, 2H, <sup>3</sup>J<sub>HH</sub> = 2.2 Hz),

7.14 (dd, 2H, ArH,  $^3J_{\text{HH}} = 2.0, 6.4$  Hz), 6.64 (d, ArH, 2H,  $^3J_{\text{HH}} = 8.3$  Hz), 6.60 (br, 2H, NH), 3.88 (s, 6H, OCH<sub>3</sub>), 3.87 (s, 6H, OCH<sub>3</sub>), 3.54 (q, 4H, CH<sub>2</sub>,  $^3J_{\text{HH}} = 5.5$  Hz), 2.73 (t, 4H, CH<sub>2</sub>,  $^3J_{\text{HH}} = 5.9$  Hz), 2.52 (t, 2H, CH<sub>2</sub>,  $^3J_{\text{HH}} = 7.2$  Hz), 1.51-1.19 (m, 12H, CH<sub>2</sub>), 0.85 (t, 3H, CH<sub>3</sub>,  $^3J_{\text{HH}} = 6.9$  Hz) ppm; <sup>13</sup>C NMR: (68 MHz, CDCl<sub>3</sub>):  $\delta$  167, 152, 149, 127, 119, 111, 110, 56, 56, 54, 53, 38, 32, 30, 29, 28, 28, 23, 14 ppm; MS (ES<sup>+</sup>): 544 [M+H]<sup>+</sup>, 566 [M+Na]<sup>+</sup>; IR (solid, cm<sup>-1</sup>): 2680 ( $\nu_{\text{(NH)}}$ ), 1586 ( $\nu_{\text{(C=O)}}$ ), 1507 ( $\nu_{\text{(Ar)}}$ ); Anal. Calc. for C<sub>30</sub>H<sub>45</sub>N<sub>3</sub>O<sub>6</sub>: C, 66.27; H, 8.34; N, 7.73. Found: C, 66.15; H, 8.30; N, 7.85.

*Compound L<sup>9</sup>*: Amine **3**<sup>8</sup> (0.40 mmol) was dissolved in water (25 cm<sup>3</sup>) containing NaOH (1.20 mmol). 3,5-Dimethoxylbenzoyl chloride (0.88 mmol) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (25 cm<sup>3</sup>) and added slowly to the amine solution. The reaction was stirred at room temperature overnight. The organic layer was separated, dried with MgSO<sub>4</sub>, filtered and the solvent removed to give a yellow oil, which was purified by column chromatography on silica gel using 96% CH<sub>2</sub>Cl<sub>2</sub>, 4% MeOH to afford the desired product as a white powder. Yield: 67%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  6.85 (d, ArH, 4H,  $^3J_{\text{HH}} = 2.4$  Hz), 6.83 (br, NH, 2H), 6.50 (t, 2H, ArH,  $^3J_{\text{HH}} = 2.4$  Hz), 3.75 (s, 12H, OCH<sub>3</sub>), 3.57 (q, 4H, CH<sub>2</sub>,  $^3J_{\text{HH}} = 5.4$  Hz), 2.76 (t, 4H, CH<sub>2</sub>,  $^3J_{\text{HH}} = 5.4$  Hz), 2.57 (t, 2H, CH<sub>2</sub>,  $^3J_{\text{HH}} = 7.5$  Hz), 1.53-1.13 (m, 12H, CH<sub>2</sub>), 0.87 (t, 3H, CH<sub>3</sub>,  $^3J_{\text{HH}} = 6.9$  Hz) ppm; <sup>13</sup>C NMR: (68 MHz, CDCl<sub>3</sub>):  $\delta$  168, 161, 137, 105, 104, 55, 54, 53, 38, 32, 30, 29, 28, 27, 23, 14 ppm; MS (ES<sup>+</sup>): 544 [M+H]<sup>+</sup>, 566 [M+Na]<sup>+</sup>; IR (solid, cm<sup>-1</sup>): 2682 ( $\nu_{\text{(NH)}}$ ), 1590 ( $\nu_{\text{(C=O)}}$ ), 1503 ( $\nu_{\text{(Ar)}}$ ); Anal. Calc. for C<sub>30</sub>H<sub>45</sub>N<sub>3</sub>O<sub>6</sub>: C, 66.27; H, 8.34; N, 7.73. Found: C, 65.93; H, 8.22; N, 7.41.

*Compound L<sup>10</sup>*: Amine **3**<sup>8</sup> (0.12 mmol) was dissolved in anhydrous THF (10 cm<sup>3</sup>). A solution of 3, 4-Dimethoxybenzenesulfonyl chloride (0.25 mmol) and triethylamine (0.70

mmol) in anhydrous THF (10 cm<sup>3</sup>) was added drop-wise with stirring at room temperature to the amine solution. A white precipitate formed immediately on mixing the two solutions. The reaction mixture was left to stir at room temperature overnight. The precipitate was filtered and the solvent removed from the mother liquor to give a yellow oil, which was purified by column chromatography on silica gel using 60% EtOAc, 40% *n*-hexane to afford the desired product as a white powder. Yield: 81%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.52 (dd, ArH, 2H, <sup>3</sup>J<sub>HH</sub> = 2.2, 6.2 Hz), 7.38 (d, 2H, ArH, <sup>3</sup>J<sub>HH</sub> = 2.2 Hz), 6.67 (d, ArH, 2H, <sup>3</sup>J<sub>HH</sub> = 8.6 Hz), 4.99 (br, 2H, NH), 3.96 (s, 6H, OCH<sub>3</sub>), 3.95 (s, 6H, OCH<sub>3</sub>), 2.94 (t, 4H, CH<sub>2</sub>, <sup>3</sup>J<sub>HH</sub> = 5.5 Hz), 2.50 (t, 4H, CH<sub>2</sub>, <sup>3</sup>J<sub>HH</sub> = 5.3 Hz), 2.25 (t, 2H, CH<sub>2</sub>, <sup>3</sup>J<sub>HH</sub> = 7.4 Hz), 1.29-1.23 (m, 12H, CH<sub>2</sub>), 0.89 (t, 3H, CH<sub>3</sub>, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz) ppm; <sup>13</sup>C NMR: (68 MHz, CDCl<sub>3</sub>): δ 152, 149, 131, 121, 110, 110, 56, 56, 53, 53, 40, 32, 29, 29, 27, 26, 23, 14 ppm; MS (ES<sup>+</sup>): *m/z* 616 [M+H]<sup>+</sup>, 638 [M+Na]<sup>+</sup>; IR (solid, cm<sup>-1</sup>): 2788 (ν<sub>(NH)</sub>), 1584 (ν<sub>(C=O)</sub>), 1503 (ν<sub>(Ar)</sub>); Anal. Calc. for C<sub>28</sub>H<sub>45</sub>N<sub>3</sub>O<sub>8</sub>S<sub>2</sub>: C, 54.61; H, 7.37; N, 6.82. Found: C, 54.53; H, 7.42; N, 6.70.

*Compound L<sup>II</sup>*: *N,N*-bis(3-aminopropyl)-methylaniline (0.20 cm<sup>3</sup>, 1.24 mmol) dissolved in dry THF (30 cm<sup>3</sup>) was added to phenyl isocyanate (0.30 g, 2.48 mmol). The reaction stirred at r.t for 2h and the solvent removed *in vacuo* to give an oily residue which was washed with a portion of Et<sub>2</sub>O and MeOH to give a white solid which was dried *in vacuo*. Yield: 80%. <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>): δ/ppm 7.90 (br, 2H, NH), 7.31 (d, 4H, <sup>3</sup>J<sub>HH</sub> = 7.6, H<sub>Ar</sub>), 7.16 (t, 4H, <sup>3</sup>J<sub>HH</sub> = 8.1, H<sub>Ar</sub>), 6.88 (t, 2H, <sup>3</sup>J<sub>HH</sub> = 7.9, H<sub>Ar</sub>), 6.35 (br, 2H, NH), 3.20 (t, 4H, <sup>3</sup>J<sub>HH</sub> = 5.9, CH<sub>2</sub>), 2.48 (t, 4H, <sup>3</sup>J<sub>HH</sub> = 5.8, CH<sub>2</sub>), 2.23 (s, 3H, NCH<sub>3</sub>), 1.60 – 1.56 (m, 4H, CH<sub>2</sub>), <sup>13</sup>C NMR (75 MHz, CD<sub>3</sub>OD): δ/ppm 156, 140, 127, 122, 118, 56, 40, 36, 25. MS(ES<sup>+</sup>): *m/z* 384 [M+H]<sup>+</sup>. IR (solid cm<sup>-1</sup>): 3319 (ν<sub>(N-H)</sub>), 2963 (ν<sub>(N-H)</sub>), 1637

( $\nu_{\text{C=O}}$ ), 1571 ( $\nu_{\text{C=C, Ar}}$ ), 752 ( $\nu_{\text{C-H, Ar}}$ ). Anal. calc. for  $\text{C}_{21}\text{H}_{29}\text{N}_5\text{O}_2$ : C, 65.76; H, 7.64; N, 18.26. Found: C, 65.77; H, 7.60; N, 18.18%.

*Compound L<sup>12</sup>*: *N,N*-bis(3-aminopropyl)-methylamine (0.15 cm<sup>3</sup>, 0.96 mmol) was dissolved in  $\text{CH}_2\text{Cl}_2$  (30 cm<sup>3</sup>). 3, 4, 5-Trimethoxyphenyl isocyanate (0.40 g, 1.91 mmol) was added and the reaction stirred at r.t. for 24 h.  $\text{H}_2\text{O}$  (15 cm<sup>3</sup>) was added to the reaction to remove the unreacted amine and isocyanate and the aqueous layer was washed with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 10$  cm<sup>3</sup>). The organic fractions were collected, dried over  $\text{MgSO}_4$ , filtered and the solvent removed to give colourless foam. Yield: 59%. <sup>1</sup>H NMR (270 MHz,  $\text{CDCl}_3$ ):  $\delta$ /ppm 8.26 (s, 2H, NH), 6.66 (t, 2H, <sup>3</sup>*J*<sub>HH</sub> = 6.2 Hz, NH), 6.61 (s, 4H, H<sub>Ar</sub>), 3.69 (s, 6H, OMe), 3.56 (s, 12H, OMe), 3.30 (br, 4H, CH<sub>2</sub>), 2.31 (br, 4H, CH<sub>2</sub>), 2.11 (s, 3H, CH<sub>3</sub>), 1.57 (br, 4H, CH<sub>2</sub>). <sup>13</sup>C NMR (68 MHz,  $\text{CDCl}_3$ ):  $\delta$ /ppm 157, 153, 136, 133, 96, 61, 56, 54, 42, 38, 27. MS ( $\text{ES}^+$ ): calc for  $\text{C}_{27}\text{H}_{42}\text{N}_5\text{O}_8$  *m/z* 564.3033, found *m/z* 564.3032 corresponds to  $[\text{M}+\text{H}]^+$ . IR (solid cm<sup>-1</sup>): 3328 ( $\nu_{\text{N-H}}$ ), 1652 ( $\nu_{\text{C=O}}$ ), 1603 ( $\nu_{\text{C=C, Ar}}$ ), 1123 ( $\nu_{\text{C-O}}$ ). Anal. Calc for  $\text{C}_{27}\text{H}_{41}\text{N}_5\text{O}_8$ : C, 57.54, H, 7.33; N, 12.43. Found: C, 57.47; H, 7.18; N, 12.32%.

*Compound L<sup>13</sup>*: 3, 3'- Diamino-*N*-methyldipropylamine (0.19 cm<sup>3</sup>, 1.15 mmol) was dissolved in  $\text{CH}_2\text{Cl}_2$  containing NaOH (0.10 g, 2.30 mmol). 3, 4, 5-Trimethoxybenzoyl chloride (0.53 g, 2.29 mol) was added and the reaction was stirred at r.t. for 20 h.  $\text{H}_2\text{O}$  (20 cm<sup>3</sup>) was added to dissolve the NaOH and the reaction stirred for a further hour. The layers were separated and the aqueous layer washed with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 10$  cm<sup>3</sup>). The organic fractions were combined, dried over  $\text{MgSO}_4$ , filtered and then the solvent removed *in vacuo* to give a colourless foam. Yield: 62%. <sup>1</sup>H NMR (270 MHz,  $\text{CDCl}_3$ ):  $\delta$ /ppm 7.69 (t, 2H, <sup>3</sup>*J*<sub>HH</sub> = 5.2 Hz, NH), 7.00 (s, 2H, H<sub>Ar</sub>), 3.82 (s, 6H, OMe), 3.77 (s, 12H,

OMe), 3.40 (dd, 4H,  $^3J_{\text{HH}} = 6.3$  Hz, 5.64 Hz,  $\text{CH}_2$ ), 2.40 (t, 4H,  $^3J_{\text{HH}} = 6.35$  Hz,  $\text{CH}_2$ ), 2.20 (s, 3H,  $\text{CH}_3$ ), 1.74 – 1.66 (m, 4H,  $\text{CH}_2$ ).  $^{13}\text{C}$  NMR (68 MHz,  $\text{CDCl}_3$ ):  $\delta$ /ppm 167, 153, 141, 130, 104, 61, 56, 55, 42, 39, 29. MS ( $\text{ES}^+$ ): calc. for  $\text{C}_{27}\text{H}_{40}\text{N}_3\text{O}_8$   $m/z$  534.2822, found  $m/z$  534.2815 corresponds to  $[\text{M}+\text{H}]^+$ . IR (solid,  $\text{cm}^{-1}$ ): 3289 ( $\nu_{\text{(N-H)}}$ ), 1630 ( $\nu_{\text{(C=O)}}$ ), 1581 ( $\nu_{\text{(C=C, Ar)}}$ ), 1123 ( $\nu_{\text{(C-O)}}$ ). Anal. calc. for  $\text{C}_{27}\text{H}_{39}\text{N}_3\text{O}_8$ : C, 60.77; H, 7.27; N, 7.87. Found: C, 60.62; H, 7.29; N, 7.81%.

*N*-[2-(Di-*n*-octylamino)ethyl]acetamide, **4**:<sup>6</sup> *N*-(2-Aminoethyl)acetamide (0.10 mol), *n*-octyl bromide (0.20 mol) and  $\text{NaHCO}_3$  were dissolved in ethanol (50  $\text{cm}^3$ ) and refluxed for 145 h. The mixture was cooled to room temperature and chloroform (50  $\text{cm}^3$ ) was added. The mixture was then filtered to remove unreacted  $\text{NaHCO}_3$ . The mother liquor was washed with water, the organic layer separated, dried with  $\text{MgSO}_4$  and solvent removed to give a light yellow oil, which was purified by column chromatography on silica gel using 70% EtOAc, 30% *n*-hexane to afford the desired product as a pale yellow oil. Yield: 67%.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  6.10 (br, 1H, NH), 3.27 (q, 2H,  $\text{CH}_2$ ,  $^3J_{\text{HH}} = 5.8$  Hz), 2.51 (t, 2H,  $\text{CH}_2$ ,  $^3J_{\text{HH}} = 6.3$  Hz), 2.39 (t, 4H,  $\text{CH}_2$ ,  $^3J_{\text{HH}} = 8.4$  Hz), 1.98 (s, 3H,  $\text{CH}_3$ ), 1.46-1.28 (m, 24H,  $\text{CH}_2$ ), 0.89 (t, 3H,  $\text{CH}_3$ ,  $^3J_{\text{HH}} = 7.7$  Hz) ppm. MS ( $\text{ES}^+$ ): 327  $[\text{M}+\text{H}]^+$ , 349  $[\text{M}+\text{Na}]^+$ . Anal. Calcd. for  $\text{C}_{20}\text{H}_{42}\text{N}_2\text{O}$ : C, 73.56; H, 12.96; N, 8.58. Found: C, 73.41; H, 13.00; N, 8.74.

*N,N*-Di-*n*-octyl-1,2-ethanediamine, **5**:<sup>6</sup> **4** (15 mol) was refluxed in a mixture of ethanol (50  $\text{cm}^3$ ) and 10 M NaOH (40  $\text{cm}^3$ ) for 3 days. The reaction mixture was cooled to room temperature. A yellow layer separated, which was collected and washed with  $\text{CH}_2\text{Cl}_2$  (50  $\text{cm}^3$ ). This caused an aqueous layer to separate. The organic layer was collected, washed with water (50  $\text{cm}^3$ ), dried with  $\text{MgSO}_4$ , filtered and the solvent removed to give a yellow

oil. Yield: 96%.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.71 (t, 2H,  $\text{CH}_2$ ,  $^3J_{\text{HH}} = 6.9$  Hz), 2.44 (t, 2H,  $\text{CH}_2$ ,  $^3J_{\text{HH}} = 7.0$  Hz), 2.38 (t, 2H,  $\text{CH}_2$ ,  $^3J_{\text{HH}} = 8.4$  Hz), 1.44-1.22 (m, 24H,  $\text{CH}_2$ ), 0.89 (t, 2H,  $\text{CH}_3$ ,  $^3J_{\text{HH}} = 7.7$  Hz), ppm. MS ( $\text{ES}^+$ ): 285  $[\text{M}+\text{H}]^+$ , 307  $[\text{M}+\text{Na}]^+$ . Anal. Calcd. for  $\text{C}_{18}\text{H}_{40}\text{N}_2$ : C, 75.98; H, 14.17; N, 9.85. Found: C, 75.24; H, 13.70; N, 9.48.

*Compound L<sup>14</sup>*: Amine **5<sup>9</sup>** (1.76 mmol) was dissolved in anhydrous THF (10  $\text{cm}^3$ ) under  $\text{N}_2$  and a solution of 3,4-dimethoxyphenyl isocyanate (1.76 mmol) dissolved in anhydrous THF (10  $\text{cm}^3$ ) was added dropwise with stirring at room temperature. The reaction was stirred at room temperature for 5 h. The solvent was removed to give a yellow oil, which was purified by column chromatography on silica gel using 94% EtOAc, 6% MeOH to afford the desired product as a white solid. Yield: 76%.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.05 (d, 1H, ArH,  $^3J_{\text{HH}} = 1.1$  Hz), 6.78-6.69 (m, 2H, ArH), 5.59 (br, 1H, NH), 3.84 (s, 6H,  $\text{OCH}_3$ ), 3.27 (q, 2H,  $\text{CH}_2$ ,  $^3J_{\text{HH}} = 5.8$  Hz), 2.55 (t, 2H,  $\text{CH}_2$ ,  $^3J_{\text{HH}} = 6.0$  Hz), 2.40 (t, 4H,  $\text{CH}_2$ ,  $^3J_{\text{HH}} = 8.7$  Hz), 1.42-1.17 (m, 24H,  $\text{CH}_2$ ), 0.86 (t, 6H,  $\text{CH}_3$ ,  $^3J_{\text{HH}} = 7.7$  Hz) ppm;  $^{13}\text{C}$  NMR: (68 MHz,  $\text{CDCl}_3$ ):  $\delta$  157, 149, 146, 132, 114, 112, 107, 56, 56, 54, 39, 32, 29, 29, 27, 27, 23, 14 ppm; MS ( $\text{ES}^+$ ): 464  $[\text{M}+\text{H}]^+$ , 484  $[\text{M}+\text{Na}]^+$ ; IR (Nujol,  $\text{cm}^{-1}$ ): 3346 ( $\nu_{\text{(NH)}}$ ), 1650 ( $\nu_{\text{(C=O)}}$ ), 1609 ( $\nu_{\text{(Ar)}}$ ); Anal. Calcd. for  $\text{C}_{27}\text{H}_{49}\text{N}_3\text{O}_3$ : C, 69.94; H, 10.65; N, 9.06. Found: C, 69.76; H, 10.68; N, 8.77.

*Compound L<sup>15</sup>*: Amine **5<sup>9</sup>** (1.76 mmol) was dissolved in anhydrous THF (10  $\text{cm}^3$ ) under  $\text{N}_2$  and a solution of 3,5-dimethoxyphenyl isocyanate (1.76 mmol) dissolved in anhydrous THF (10  $\text{cm}^3$ ) was added dropwise with stirring at room temperature. The reaction was stirred at room temperature for 5 h. The solvent was removed to give a yellow oil, which was purified by column chromatography on silica gel using 94% EtOAc, 6% MeOH to afford the desired product as a white solid. Yield: 97%.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$



6.59 (d, 2H, ArH,  $^3J_{\text{HH}} = 2.7$  Hz), 6.17 (t, 1H, ArH,  $^3J_{\text{HH}} = 2.7$  Hz), 3.77 (s, 6H, OCH<sub>3</sub>), 3.35 (q, 2H, CH<sub>2</sub>,  $^3J_{\text{HH}} = 5.4$  Hz), 2.70 (t, 2H, CH<sub>2</sub>,  $^3J_{\text{HH}} = 5.4$  Hz), 2.56 (t, 4H, CH<sub>2</sub>,  $^3J_{\text{HH}} = 8.1$  Hz), 1.52-1.21 (m, 24H, CH<sub>2</sub>), 0.88 (t, 6H, CH<sub>3</sub>,  $^3J_{\text{HH}} = 8.1$  Hz) ppm; <sup>13</sup>C NMR: (68 MHz, CDCl<sub>3</sub>): δ 161, 141, 98, 96, 55, 54, 39, 32, 30, 29, 28, 27, 26, 23, 14 ppm; MS (ES<sup>+</sup>): 464 [M+H]<sup>+</sup>; IR (Nujol, cm<sup>-1</sup>): 3340 (ν<sub>(NH)</sub>), 1652 (ν<sub>(C=O)</sub>), 1614 (ν<sub>(Ar)</sub>); Anal. Calcd. for C<sub>27</sub>H<sub>49</sub>N<sub>3</sub>O<sub>3</sub>: C, 69.94; H, 10.65; N, 9.06. Found: C, 69.46; H, 10.77; N, 9.02.

*Compound L<sup>16</sup>*: Amine **5**<sup>9</sup> (1.05 mmol) was dissolved in water (10 cm<sup>3</sup>) containing NaOH (2.10 mmol). 3,4-Dimethoxybenzoyl chloride (1.05 mmol) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (10 cm<sup>3</sup>) and added slowly to the amine solution. The reaction was stirred at room temperature overnight. The organic layer was separated, dried with MgSO<sub>4</sub>, filtered and solvent removed to give a yellow oil, which was purified by column chromatography on silica gel using 98% EtOAc, 2% MeOH to afford the desired product as a yellow oil. Yield: 85%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.47 (d, 1H, ArH,  $^3J_{\text{HH}} = 2.1$  Hz), 7.28 (dd, 1H, ArH,  $^3J_{\text{HH}} = 2.1, 6.3$  Hz), 6.75 (d, 1H, ArH,  $^3J_{\text{HH}} = 8.4$  Hz), 3.94 (s, 3H, OCH<sub>3</sub>), 3.92 (s, 3H, OCH<sub>3</sub>), 3.56 (q, 2H, CH<sub>2</sub>,  $^3J_{\text{HH}} = 5.1$  Hz), 2.64 (t, 2H, CH<sub>2</sub>,  $^3J_{\text{HH}} = 5.7$  Hz), 2.46 (t, 4H, CH<sub>2</sub>,  $^3J_{\text{HH}} = 7.5$  Hz), 1.48-1.25 (m, 24H, CH<sub>2</sub>), 0.87 (t, 6H, CH<sub>3</sub>,  $^3J_{\text{HH}} = 6.9$  Hz) ppm; <sup>13</sup>C NMR: (75 MHz, CDCl<sub>3</sub>): δ 167, 152, 149, 127, 119, 111, 110, 58, 56, 53, 37, 32, 29, 28, 27, 23, 14 ppm; MS (ES<sup>+</sup>): 449 [M+H]<sup>+</sup>, 471 [M+Na]<sup>+</sup>; IR (Nujol, cm<sup>-1</sup>): 3337 (ν<sub>(NH)</sub>), 1637 (ν<sub>(C=O)</sub>), 1604 (ν<sub>(Ar)</sub>); Anal. Calc. for C<sub>27</sub>H<sub>48</sub>N<sub>2</sub>O<sub>3</sub>: C, 72.28; H, 10.78; N, 6.24. Found: C, 71.96; H, 10.88; N, 6.03.

*Compound L<sup>17</sup>*: Amine **5**<sup>9</sup> (4.00 mmol) was dissolved in water (40 cm<sup>3</sup>) containing NaOH (4.40 mmol). 3,5-Dimethoxybenzoyl chloride (4.0 mmol) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (10 cm<sup>3</sup>) and added slowly to the amine solution. The reaction was stirred at

room temperature overnight. The organic layer was separated, dried with  $\text{MgSO}_4$ , filtered and solvent removed to give a yellow oil, which was purified by column chromatography on silica gel using 98% EtOAc, 2% MeOH to afford the desired product as a yellow oil. Yield: 81%.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  6.95 (d, 2H, ArH,  $^3J_{\text{HH}} = 2.7$  Hz), 6.57 (t, 1H, ArH,  $^3J_{\text{HH}} = 2.7$  Hz), 3.82 (s, 6H,  $\text{OCH}_3$ ), 3.51 (q, 2H,  $\text{CH}_2$ ,  $^3J_{\text{HH}} = 5.4$  Hz), 2.70 (t, 2H,  $\text{CH}_2$ ,  $^3J_{\text{HH}} = 5.4$  Hz), 2.50 (t, 4H,  $\text{CH}_2$ ,  $^3J_{\text{HH}} = 8.1$  Hz), 1.47-1.24 (m, 24H,  $\text{CH}_2$ ), 0.87 (t, 6H,  $\text{CH}_3$ ,  $^3J_{\text{HH}} = 6.6$  Hz) ppm;  $^{13}\text{C}$  NMR: (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  167, 161, 137, 107, 105, 103, 55, 54, 52, 37, 32, 30, 29, 27, 27, 23, 14 ppm; MS ( $\text{ES}^+$ ): 449  $[\text{M}+\text{H}]^+$ , 471  $[\text{M}+\text{Na}]^+$ ; IR (Nujol,  $\text{cm}^{-1}$ ): 3336 ( $\nu_{\text{NH}}$ ), 1645 ( $\nu_{\text{C=O}}$ ), 1595 ( $\nu_{\text{Ar}}$ ); Anal. Calc. for  $\text{C}_{27}\text{H}_{48}\text{N}_2\text{O}_3$ : C, 72.28; H, 10.78; N, 6.24. Found: C, 71.78; H, 10.34; N, 6.11.

*Compound L<sup>18</sup>*: Amine **5<sup>9</sup>** (1.05 mmol) was dissolved in anhydrous THF (10  $\text{cm}^3$ ) and a solution of 3, 4- dimethoxybenzene sulfonyl chloride (1.05 mmol) and triethylamine (3.16 mmol) in anhydrous THF (10  $\text{cm}^3$ ) was added to the amine solution. A white precipitate formed immediately on mixing the two solutions. The reaction mixture was left to stir at room temperature overnight. The precipitate was filtered and the solvent removed from the mother liquor to give a yellow oil, which was purified by column chromatography on silica gel using 75% EtOAc, 25% *n*-hexane to afford the desired product as a yellow oil. Yield: 98%.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.49 (dd, 1H, ArH,  $^3J_{\text{HH}} = 2.1, 6.3$  Hz), 7.35 (d, 1H, ArH,  $^3J_{\text{HH}} = 2.1$  Hz), 6.64 (d, 1H, ArH,  $^3J_{\text{HH}} = 8.4$  Hz), 3.96 (s, 3H,  $\text{OCH}_3$ ), 3.95 (s, 3H,  $\text{OCH}_3$ ), 3.56 (t, 2H,  $\text{CH}_2$ ,  $^3J_{\text{HH}} = 5.4$  Hz), 2.48 (t, 2H,  $\text{CH}_2$ ,  $^3J_{\text{HH}} = 5.4$  Hz), 2.26 (t, 4H,  $\text{CH}_2$ ,  $^3J_{\text{HH}} = 7.5$  Hz), 1.36-1.16 (m, 24H,  $\text{CH}_2$ ), 0.91 (t, 6H,  $\text{CH}_3$ ,  $^3J_{\text{HH}} = 7.2$  Hz) ppm;  $^{13}\text{C}$  NMR: (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  152, 149, 131, 121, 110, 110, 56, 56, 54, 52, 40, 32, 30, 29, 27, 27, 23, 14 ppm; MS ( $\text{ES}^+$ ):  $m/z$  485  $[\text{M}+\text{H}]^+$ , 507

[M+Na]<sup>+</sup>; IR (Nujol, cm<sup>-1</sup>): 3281 (ν<sub>(NH)</sub>), 1590 (ν<sub>(C=O)</sub>), 1510 (ν<sub>(Ar)</sub>); Anal. Calc. for C<sub>26</sub>H<sub>48</sub>N<sub>2</sub>SO<sub>4</sub>: C, 64.42; H, 9.98; N, 5.78. Found: C, 64.12; H, 9.93; N, 5.48.

*Methyl 3-(di-2-ethylhexylamino)propanoate, 6*: A solution of di-2-ethylhexylamine (19.9 mmol) and methyl acrylate (40.0 mmol) in MeOH (40 cm<sup>3</sup>) was stirred at room temperature for 24 hr. The solvent was removed using a rotary evaporator and the product purified by column chromatography on silica gel using 10% EtOAc, 90% hexane to afford the desired product as a colourless oil. Yield: 67 % yield. <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>): δ 3.88 (s, 3H, OCH<sub>3</sub>), 2.87 (t, 2H, NCH<sub>2</sub>CH<sub>2</sub>), 2.63 (t, 2H, CH<sub>2</sub>CO), 2.34 (d, 4H, CHCH<sub>2</sub>N), 1.35-1.67 (m, 18H, (CH<sub>2</sub>)<sub>3</sub>CHCH<sub>2</sub>), 0.95-1.18 (m, 12H, CH<sub>3</sub>); <sup>13</sup>C NMR (68 MHz, CDCl<sub>3</sub>) ppm: δ 174, 60, 52, 51, 38, 33, 32, 29, 25, 24, 14, 11 ppm; IR (thin film, cm<sup>-1</sup>): (ν<sub>(CH)</sub>) 2860-2957, (ν<sub>(C=O)</sub>) 1743, (ν<sub>(CH)</sub>) 1456-1400, (ν<sub>(CN)</sub>) 1194, (ν<sub>(OMe)</sub>) 1033.

*Compound L<sup>19</sup>*: Methyl 3-(di-2-ethylhexylamino)propanoate,<sup>18</sup> **6** (13.0 mmol) was dissolved in hexylamine (64.9 mmol) and heated at 85°C for 24 hr. The hexylamine was removed under vacuum and the residue purified by column chromatography on silica gel using 50% EtOAc, 50% hexane to afford the desired product as a pale yellow oil. Yield: 68 %. <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>): δ 7.85 (t, 1H, NH<sub>2</sub>), 3.02-3.20 (m, 2H, NHCH<sub>2</sub>), 2.45 (t, 2H, NCH<sub>2</sub>), 2.25 (d, 4H, NCH<sub>2</sub>), 2.07 (t, 2H, COCH<sub>2</sub>), 1.30-1.50 (m, 2H, CH<sub>2</sub>), 0.95-1.30 (m, 24H, CH<sub>2</sub>,CH), 0.49-0.95 (m, 15H, CH<sub>3</sub>) ppm; <sup>13</sup>C NMR (68 MHz, CDCl<sub>3</sub>) δ 173, 59, 51, 40, 37, 34, 32, 32, 30, 29, 27, 25, 24, 23, 14, 14, 11 ppm; IR (thin film, cm<sup>-1</sup>): (ν<sub>(NH)</sub>) 3290, (ν<sub>(CH)</sub>) 2957-2813, (ν<sub>(C=O)</sub>) 1644, (ν<sub>(NH)</sub>) 1557, (ν<sub>(CH)</sub>) 1462-1377.

*Dimethyl 3,3'-(2-ethylhexylimino)dipropanoate,<sup>18</sup> 7*: A solution of 2-ethylhexylamine (19.4 mmol) and methyl acrylate (59.4 mmol) in MeOH (40 cm<sup>3</sup>) was stirred at room temperature for 24 hr. The solvent was removed using a rotary evaporator and the product

purified by column chromatography on silica gel using 10% EtOAc, 90% hexane to afford the desired product as colourless oil. Yield: 74 %.  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ):  $\delta$  3.44 (s, 6H,  $\text{OCH}_3$ ), 2.54 (t, 4H,  $\text{NCH}_2\text{CH}_2$ ), 2.22 (t, 4H,  $\text{CH}_2\text{CO}$ ), 2.00 (d, 2H,  $\text{CHCH}_2\text{N}$ ), 0.93-1.24 (m, 9H,  $\text{CH}_2, \text{CH}$ ), 0.59-0.73 (m, 6H,  $\text{CH}_3$ ) ppm;  $^{13}\text{C}$  NMR (68 MHz,  $\text{CDCl}_3$ )  $\delta$  173, 59, 52, 50, 37, 33, 31, 29, 24, 23, 14, 11 ppm; IR (thin film,  $\text{cm}^{-1}$ ): ( $\nu_{\text{CH}}$ ) 2956-2857, ( $\nu_{\text{C=O}}$ ) 1742, ( $\nu_{\text{CH}}$ ) 1425-1436, ( $\nu_{\text{CN}}$ ) 1195, ( $\nu_{\text{OMe}}$ ) 1042.

*Compound L<sup>20</sup>*: Dimethyl 3,3'(2-ethylhexylimino)dipropanoate **7** (16.6 mmol) was dissolved in hexylamine (133 mmol) and heated at 85°C for 24 hrs. The hexylamine was removed under vacuum and the residue purified by column chromatography on silica gel using 5% MeOH, 95% EtOAc to afford the desired product as a pale yellow oil. Yield: 66 %.  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.89-8.03 (br, 2H,  $\text{NH}$ ), 3.08-3.20 (m, 4H,  $\text{NHCH}_2$ ), 2.48 (d, 2H,  $\text{NCH}_2$ ), 2.81 (t, 4H,  $\text{NCH}_2$ ), 2.37 (t, 4H,  $\text{COCH}_2$ ), 1.30-1.48 (m, 4H,  $\text{CH}_2$ ), 0.96-1.30 (m, 21H,  $\text{CH}_2, \text{CH}$ ), 0.60-0.96 (m, 12H,  $\text{CH}_3$ ) ppm;  $^{13}\text{C}$  NMR (68 MHz,  $\text{CDCl}_3$ )  $\delta$  173, 59, 53, 40, 37, 33, 32, 31, 30, 29, 27, 25, 24, 23, 14, 14, 11 ppm; IR (thin film,  $\text{cm}^{-1}$ ): ( $\nu_{\text{NH}}$ ) 3289, ( $\nu_{\text{CH}}$ ) 2928-2804, ( $\nu_{\text{C=O}}$ ) 1643, ( $\nu_{\text{NH}}$ ) 1558, ( $\nu_{\text{CH}}$ ) 1458-1377.

*Trimethyl 3,3',3''-nitrilotripropanoate*,<sup>18</sup> **8**: A solution of 35% aqueous ammonia (21 mmol) and methyl acrylate (168 mmol) in MeOH (40  $\text{cm}^3$ ) was stirred at room temperature for 24 hr. Excess starting materials and solvent were removed under vacuum to give the product as a colourless liquid. Yield: 42%.  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ):  $\delta$  3.62 (s, 9H,  $\text{OCH}_3$ ), 2.72 (t, 6H,  $\text{NCH}_2$ ), 2.38 (t, 6H,  $\text{COCH}_2$ ) ppm;  $^{13}\text{C}$  NMR (68 MHz,  $\text{CDCl}_3$ )  $\delta$  173, 52, 49, 33 ppm; IR (thin film,  $\text{cm}^{-1}$ ): ( $\nu_{\text{CH}}$ ) 2953-2842, ( $\nu_{\text{C=O}}$ ) 1733, ( $\nu_{\text{NH}}$ ) 1558, ( $\nu_{\text{CH}}$ ) 1437, ( $\nu_{\text{CN}}$ ) 1173, ( $\nu_{\text{OMe}}$ ) 1039.

*Compound L<sup>21</sup>*: Trimethyl 3,3',3''-nitrilotripropanoate **8** (20.0 mmol) was dissolved in hexylamine (148 mmol) and heated at 85°C for 24 hrs. The hexylamine was removed under vacuum and the residue was washed with hexane yielding the desired product as a white powder. Yield: 11 %. <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>): δ 6.88-7.03 (br, 3H, NH), 3.43 (t, 6H, NCH<sub>2</sub>), 3.10 (t, 6H, NHCH<sub>2</sub>), 2.54 (t, 6H, COCH<sub>2</sub>), 1.62-1.80 (m, 6H, CH<sub>2</sub>), 1.35-1.62 (m, 18H, CH<sub>2</sub>), 0.99-1.10 (m, 9H, CH<sub>3</sub>) ppm; <sup>13</sup>C NMR (68 MHz, CDCl<sub>3</sub>) δ 173, 46, 40, 36, 32, 30, 27, 23, 14; IR (thin film, cm<sup>-1</sup>): (ν<sub>NH</sub>) 3306, (ν<sub>CH</sub>) 2925-2749, (ν<sub>C=O</sub>) 1635, (ν<sub>NH</sub>) 1547, (ν<sub>CH</sub>) 1428-1378.

*N-Methylhexylacrylamide 10*: *N*-methylhexylamine (10.8 mmol) and triethylamine (16.5 mmol) in DCM (40 mL) was cooled in an ice bath to 0°C and acryloyl chloride (11.1 mmol) in DCM (30 mL) added cautiously and the mixture stirred for 1 h. Deionised water (40 mL) was added and the aqueous phase was separated and washed with DCM (3 x 20 mL). The combined organic extracts were dried over MgSO<sub>4</sub> and reduced *in vacuo* to give **10** as a yellow paste. Yield: 80 %. <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>): δ 6.65-6.78 (m, 1H, CH), 6.37-6.50 (m, 1H, CH<sub>2</sub>), 5.74-5.85 (m, 1H, CH<sub>2</sub>), 3.41-3.60 (m, 2H, NCH<sub>2</sub>), 3.15 (d, 3H, NCH<sub>3</sub>), 1.58-1.79 (m, 2H, CH<sub>2</sub>), 1.34-1.51 (m, 6H, CH<sub>2</sub>), 0.94-1.09 (m, 3H, CH<sub>3</sub>); m/z (ES) 170.15 (M+H<sup>+</sup>).

*Compound L<sup>22</sup>*: A solution of di-2-ethylhexylamine (19.9 mmol) and **10** (18.2 mmol) in MeOH (100 mL) was heated under reflux for 24 h, concentrated on a rotary evaporator and the resulting oil purified on a silica column eluting with 4 % ethyl acetate in hexane to give the desired product as a pale yellow liquid. Yield: 59 %. <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>): δ 3.15-3.32 (m, 2H, NCH<sub>2</sub>), 2.88 (d, 3H, NCH<sub>3</sub>), 2.60-2.71 (m, 2H, NCH<sub>2</sub>CH), 2.30-2.45 (m, 2H, CHCO), 2.09 (d, 4H, CHCH<sub>2</sub>N), 1.05-1.67 (m, 18H, CH<sub>2</sub>CH), 0.66-

0.99 (m, 15H,  $CH_3$ );  $^{13}C$  NMR (68 MHz,  $CDCl_3$ ):  $\delta$  173.1, 58.9, 53.6, 41.8, 39.8, 37.0, 33.7, 32.3, 31.9, 31.1, 30.7, 28.4, 25.3, 24.6, 23.9, 13.4, 13.3, 10.1; IR (thin film,  $cm^{-1}$ ): ( $\nu_{CH}$ ) 2956-2862, ( $\nu_{C=O}$ ) 1746, ( $\nu_{CH}$ ) 1454-1401, ( $\nu_{NC}$ ) 1196, ( $\nu_{OMe}$ ) 1036; m/z (ES) 411.53 ( $M+H^+$ ). Anal. Calc. for  $C_{26}H_{54}N_2O$ : C, 76.03; H, 13.25; N, 6.82. Found: C, 76.30; H, 12.94; N, 6.97.

*Compound L<sup>23</sup>*: Methyl acrylate (70.0 mmol) and di-isobutylamine (64.9 mmol) were stirred in methanol (50 mL) for 24 h. The reaction mixture was reduced *in vacuo* and re-dissolved in butylamine (350 mmol) and heated to 90°C for 48 h. The desired product was obtained as a pale yellow oil by vacuum distillation. Yield: 78 %.  $^1H$  NMR (250 MHz,  $CDCl_3$ ):  $\delta$  8.12 (t, 1H, NH), 3.20-3.31 (q, 2H,  $CH_2$ ), 2.52-2.69 (t, 2H,  $CH_2$ ), 2.35-2.46 (t, 2H,  $CH_2$ ), 2.15-2.21 (m, 4H,  $CH_2$ ), 1.71-1.89 (m, 2H, CH), 1.21-1.59 (m, 4H,  $CH_2$ ), 0.44-0.91 (m, 15H,  $CH_3$ );  $^{13}C$  NMR (68 MHz,  $CDCl_3$ ):  $\delta$  179.7, 59.6, 52.9, 45.4, 35.9, 34.7, 30.6, 25.5, 16.6, 16.1, 14.8; IR (thin film,  $cm^{-1}$ ): ( $\nu_{NH}$ ) 3294, ( $\nu_{CH}$ ) 2954-2813, ( $\nu_{C=O}$ ) 1645, ( $\nu_{NH}$ ) 1559, ( $\nu_{CH}$ ) 1460-1373; m/z (ES) 411.53 ( $M+H^+$ ).

*Complex L<sup>4</sup>•HCl*: **L<sup>4</sup>** (1 mmol) was dissolved in anhydrous chloroform (20  $cm^3$ ), and the solution cooled to 0°C. Anhydrous hydrogen chloride gas was slowly bubbled through the solution until cloudiness was observed. The white solid was recrystallised from chloroform and dried to afford a white solid as the desired product. Yield: 80%.  $^1H$  NMR (300 MHz,  $CDCl_3$ ):  $\delta$  11.07 (s, 1H,  $NHCl$ ), 8.43 (s, 1H,  $NHCO$ ), 7.05 (d, 6H, ArH,  $^3J_{HH}$  = 2.3 Hz), 6.49 (t, 3H, ArH,  $^3J_{HH}$  = 2.3 Hz), 3.89 (bs, 6H,  $CH_2$ ), 3.76 (s, 18H,  $OCH_3$ ), 3.53 (bs, 6H,  $CH_2$ );  $^{13}C$  NMR (75 MHz,  $CDCl_3$ ):  $\delta$  169, 161, 135, 105, 104, 56, 55, 36;

Anal. Calcd. for  $C_{33}H_{43}N_4O_9Cl$ : C, 58.70; H, 6.42; N, 8.30. Found: C, 57.42; H, 6.27; N, 8.12.

*Complex  $L^9 \cdot HCl$* :  $L^9$  (1 mmol) was dissolved in anhydrous *n*-hexane (20 cm<sup>3</sup>), and the solution cooled to 0°C. Anhydrous hydrogen chloride gas was slowly bubbled through the solution until cloudiness was observed. The white solid was recrystallised from *n*-hexane and dried to afford a white solid as the desired product. Yield: 83%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  10.98 (s, 1H, *NHCl*), 8.65 (t, 2H, *NHCO*), 7.14 (d, 4H, *ArH*,  $J_{HH} = 2.3$  Hz), 6.52 (t, 2H, *ArH*,  $J_{HH} = 2.3$  Hz), 3.87 (bs, 4H, *CH*<sub>2</sub>), 3.76 (s, 12H, *OCH*<sub>3</sub>), 3.42 (bs, 4H, *CH*<sub>2</sub>), 3.21-3.10 (m, 2 H, *CH*<sub>2</sub>), 1.86-1.71 (m, 2H, *CH*<sub>2</sub>), 1.36-1.10 (m, 10H, *CH*<sub>2</sub>), 0.85 (t, 3H, *CH*<sub>3</sub>,  $J_{HH} = 6.6$  Hz); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  168, 161, 135, 106, 105, 56, 56, 55, 36, 32, 29, 27, 23, 22, 14; Anal. Calcd. for  $C_{30}H_{46}N_3O_6Cl$ : C, 66.27; H, 8.34; N, 7.73. Found: C, 65.45; H, 8.20; N, 7.36.

*Complex  $L^{17} \cdot HCl$* :  $L^{17}$  (1 mmol) was dissolved in anhydrous *n*-hexane (20 cm<sup>3</sup>), and the solution cooled to 0°C. Anhydrous hydrogen chloride gas was slowly bubbled through the solution until cloudiness was observed. The white solid was recrystallised from *n*-hexane and dried to afford a yellow oil as the desired product. Yield: 92%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  11.65 (s, 1H, *NHCl*), 8.96 (t, 1H, *NHCO*,  $J_{HH} = 5.4$  Hz), 7.29 (d, 2H, *ArH*,  $J_{HH} = 2.4$  Hz), 6.60 (t, 1H, *ArH*,  $J_{HH} = 2.4$  Hz), 3.91-3.83 (q, 2H, *CH*<sub>2</sub>, partially obscured), 3.86 (s, 6H, *OCH*<sub>3</sub>), 3.25 (q, 2H, *CH*<sub>2</sub>,  $J_{HH} = 5.1$  Hz), 3.08-2.97 (m, 4H, *CH*<sub>2</sub>), 1.88-1.17 (m, 24H, *CH*<sub>2</sub>), 0.88 (t, 6H, *CH*<sub>3</sub>,  $J_{HH} = 6.6$  Hz); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  168, 161, 136, 105, 105, 56, 55, 54, 36, 32, 29, 27, 24, 23, 14; Anal. Calcd. for  $C_{27}H_{49}N_2O_3Cl$ : C, 66.84; H, 10.18; N, 5.77. Found: C, 65.96; H, 10.38; N, 5.63.

**Complex TOA•HCl: TOA** (1 mmol) was dissolved in anhydrous *n*-pentane (20 cm<sup>3</sup>), and the solution cooled to 0°C. Anhydrous hydrogen chloride gas was slowly bubbled through the solution until cloudiness was observed. The white solid was recrystallised from *n*-pentane and dried to afford a white solid as the desired product. Yield: 66%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 11.96 (s, 1H, NHCl), 2.99-2.88 (m, 6H, -CH<sub>2</sub>), 1.86-1.68 (m, 6H, CH<sub>2</sub>), 1.40-1.16 (m, 30H, CH<sub>2</sub>), 2.40 (t, 9H, CH<sub>3</sub>, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 52, 32, 29, 28, 27, 23, 22, 14; Anal. Calcd. for C<sub>24</sub>H<sub>52</sub>NCl: C, 73.89; H, 13.43; N, 3.59. Found: C, 73.82; H, 13.39; N, 3.63.

**Platinum (IV) bis(tetraoctylammonium) chloride, 9:** A solution of K<sub>2</sub>PtCl<sub>6</sub> (0.52 mmol) in water (50 cm<sup>3</sup>) was mixed with a solution of tetraoctylammonium chloride (1.03 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (100 cm<sup>3</sup>). The mixture was stirred for 16 h at room temperature. During this time, the orange color from organic phase disappeared and organic phase became bright orange. The organic fraction was separated and the aqueous phase was washed with CH<sub>2</sub>Cl<sub>2</sub> (2x50 cm<sup>3</sup>). The combined organic extracts were dried with MgSO<sub>4</sub>, filtered and the solvent removed to afford the desired product as an orange solid. Yield: 89%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 3.37-3.22 (m, 16H, CH<sub>2</sub>), 1.69-1.51 (m, 16H, CH<sub>2</sub>), 1.46-1.14 (m, 80H, CH<sub>2</sub>), 0.85 (t, 24H, CH<sub>3</sub>, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 59, 32, 30, 29, 26, 23, 22, 14; <sup>195</sup>Pt NMR (64 MHz, CDCl<sub>3</sub>): δ (ppm) = 146. Anal. Calcd. for C<sub>64</sub>H<sub>136</sub>N<sub>2</sub>PtCl<sub>6</sub>: C, 57.30; H, 10.22; N, 2.09. Found: C, 57.58; H, 10.25; N, 2.06.

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### **Associated content**

\*S Supporting Information

The Supporting Information is available free of charge on the

ACS Publications website at .....

Solvent extraction data for **L**<sup>1</sup>, **L**<sup>2</sup>, **L**<sup>3</sup>, **L**<sup>4</sup>, **L**<sup>6</sup>, **L**<sup>7</sup>, **L**<sup>8</sup>, **L**<sup>9</sup>, **L**<sup>11</sup>, **L**<sup>12</sup>, **L**<sup>13</sup> and **L**<sup>14</sup>; additional information on crystal structures and contact distances defining intermolecular H-bonds; <sup>1</sup>H nmr data for all protons in titration of **L**<sup>4</sup>•HCl with [(Oct<sub>4</sub>N)<sub>2</sub>PtCl<sub>6</sub>].

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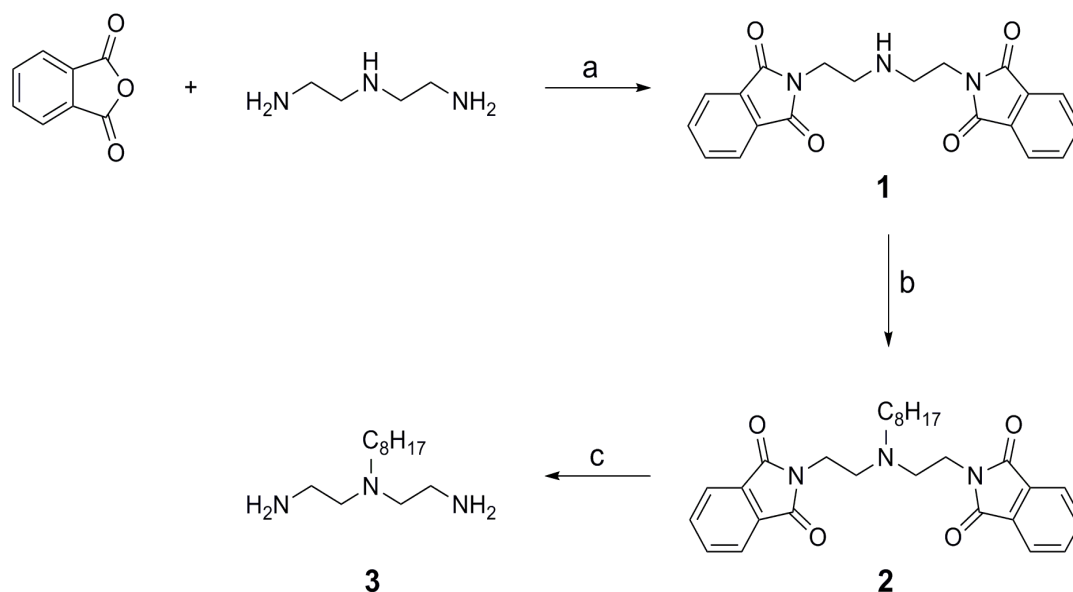
### **Author Contributions**

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

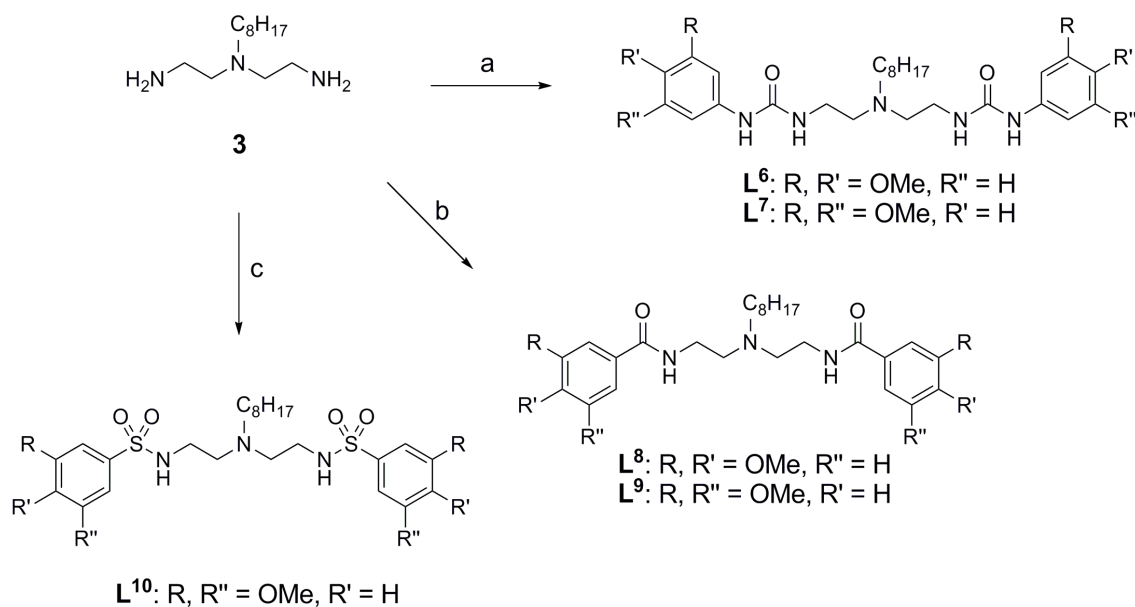
### **Notes**

The authors declare no competing financial interest.

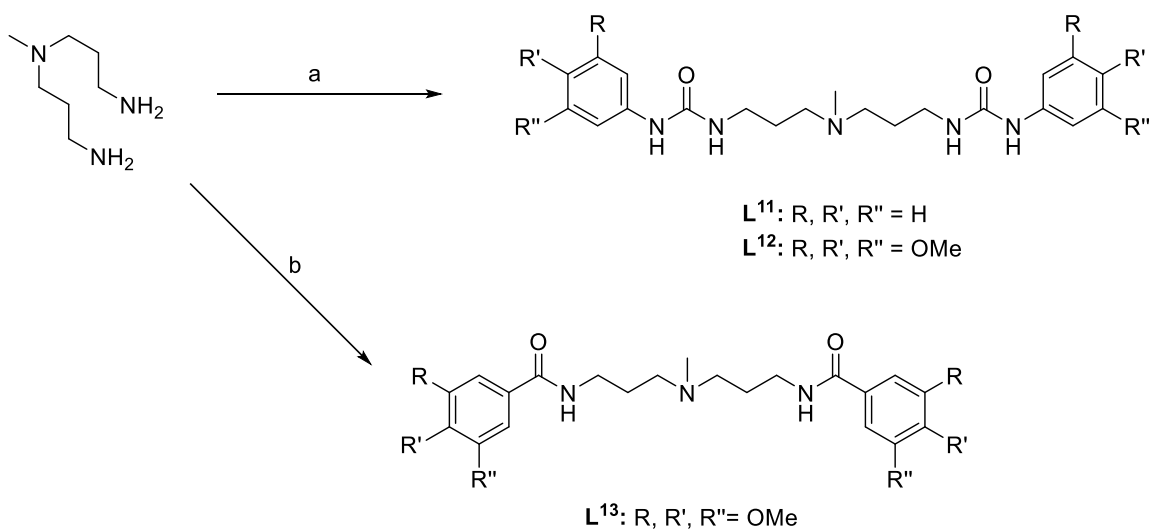
### **SCHEMES AND FIGURES**



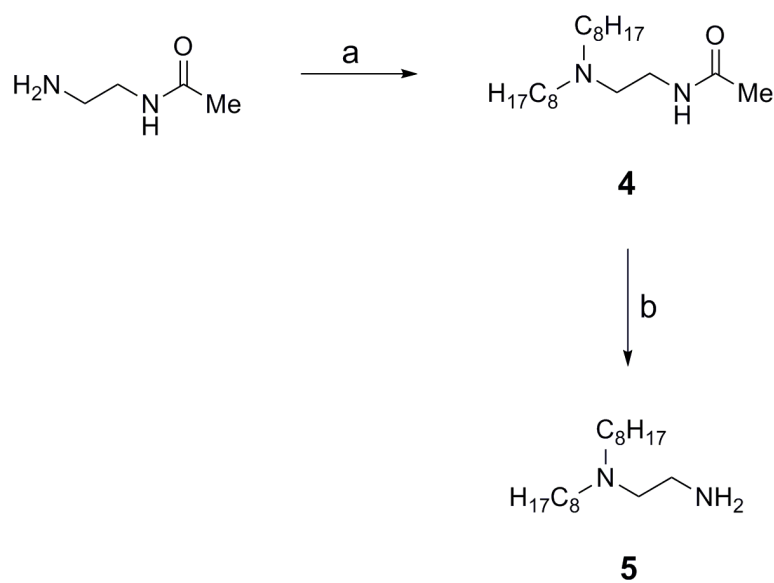
**Scheme 1.** Synthesis of amine **3**: a) AcOH, NaHCO<sub>3</sub>; b) BrC<sub>8</sub>H<sub>17</sub>, K<sub>2</sub>CO<sub>3</sub>, MeCN; c) N<sub>2</sub>H<sub>4</sub>, EtOH.<sup>5</sup>



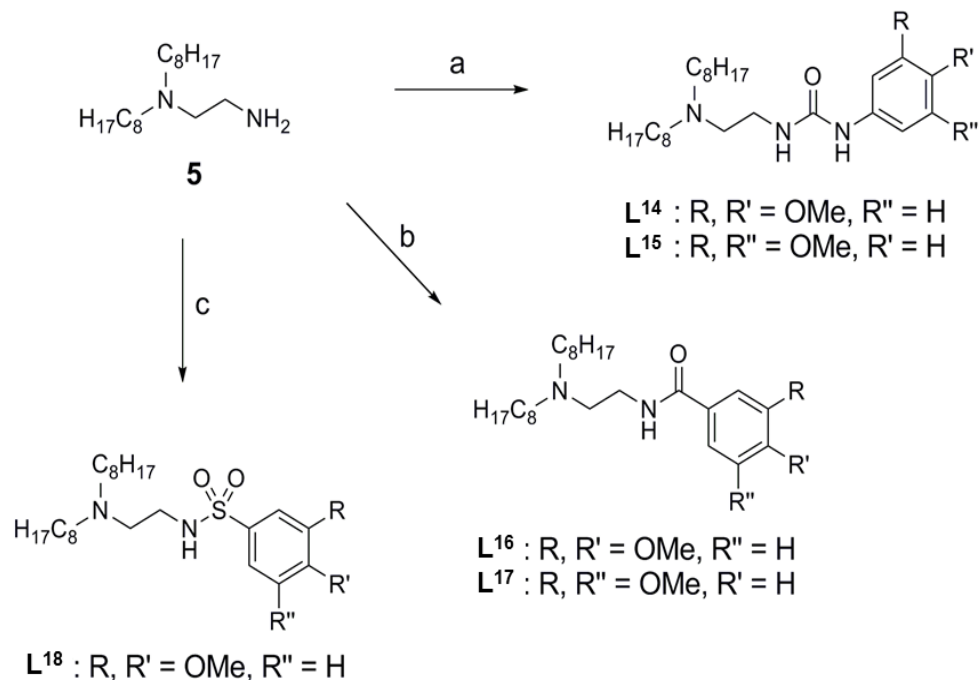
**Scheme 2.** Synthesis of receptors **L<sup>6</sup>-L<sup>10</sup>**: a) 3,4-dimethoxyphenyl isocyanate or 3,5-dimethoxyphenyl isocyanate, THF, RT; b) 3,4-dimethoxybenzoyl chloride or 3,5-dimethoxybenzoyl chloride, NaOH, H<sub>2</sub>O, CH<sub>2</sub>Cl<sub>2</sub>, RT; c) 3,4-dimethoxyphenyl sulfonyl chloride, THF, triethylamine, RT.



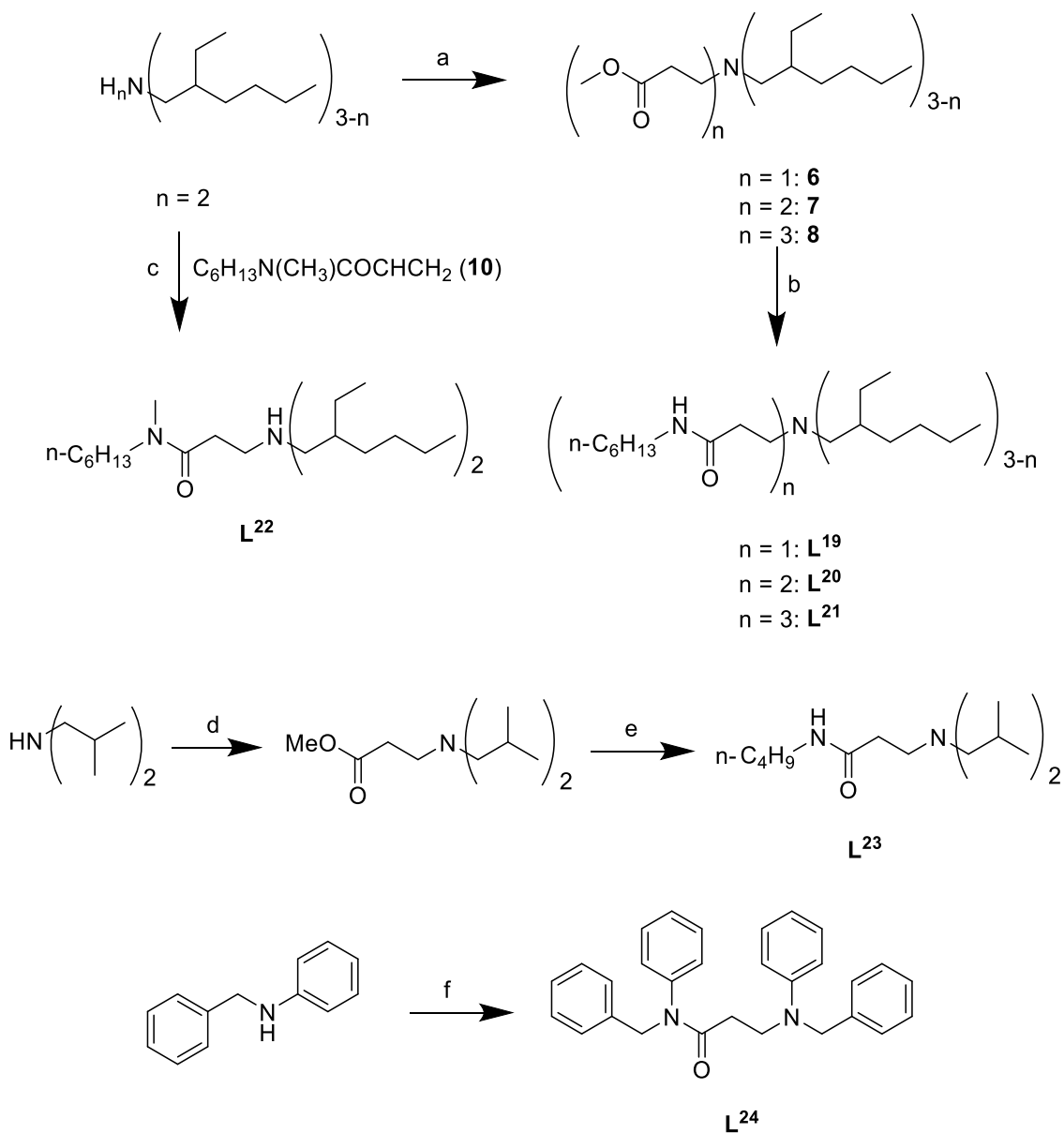
**Scheme 3.** Synthesis of receptors **L<sup>11</sup>-L<sup>13</sup>**: a) phenyl isocyanate or 3,4,5-trimethoxyphenyl isocyanate, THF, RT; b) 3,4,5-trimethoxybenzoyl chloride NaOH, H<sub>2</sub>O, CH<sub>2</sub>Cl<sub>2</sub>, RT.



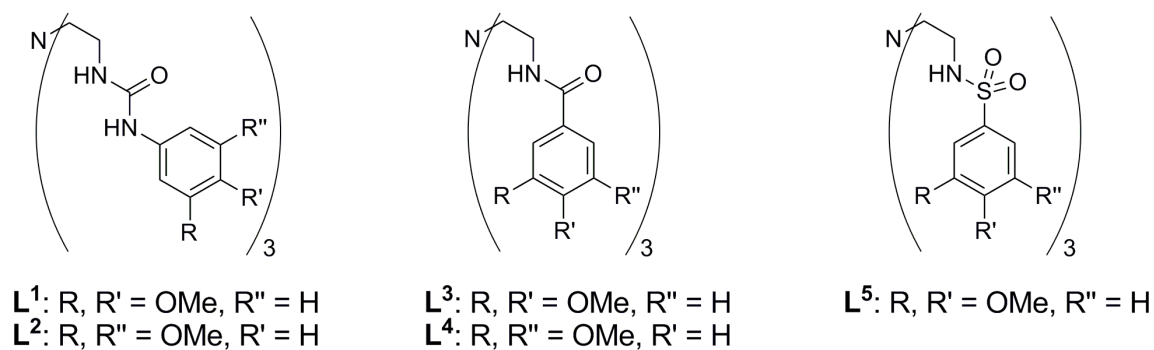
**Scheme 4.** Synthesis of amine **5**<sup>9</sup>: a) BrC<sub>8</sub>H<sub>17</sub>, EtOH, NaHCO<sub>3</sub>; b) 10M NaOH, EtOH.<sup>6</sup>



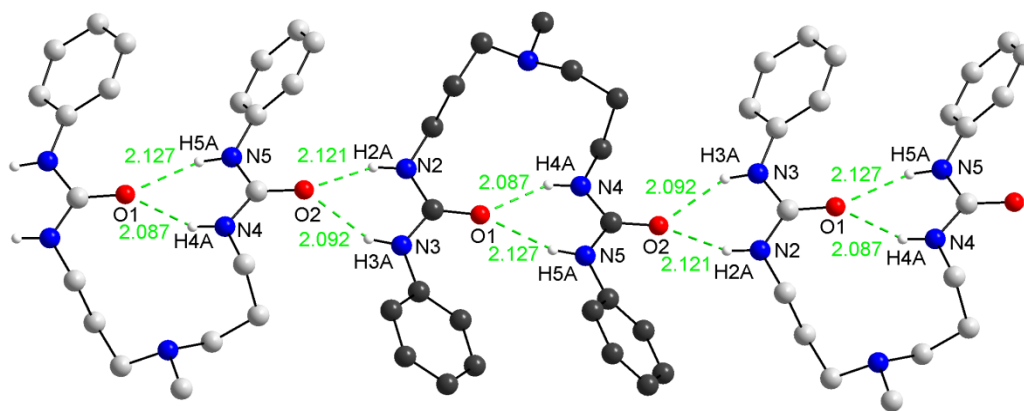
**Scheme 5.** Synthesis of receptors **L<sup>14</sup>-L<sup>18</sup>**: a) 3,4-dimethoxyphenyl isocyanate or 3,5-dimethoxyphenyl isocyanate, THF, RT; b) 3,4-dimethoxybenzoyl chloride or 3,5-dimethoxybenzoyl chloride, NaOH, H<sub>2</sub>O, CH<sub>2</sub>Cl<sub>2</sub>, RT; c) 3,4-dimethoxyphenyl sulfonyl chloride or 3,5-dimethoxyphenyl sulfonyl chloride, THF, triethylamine, RT.



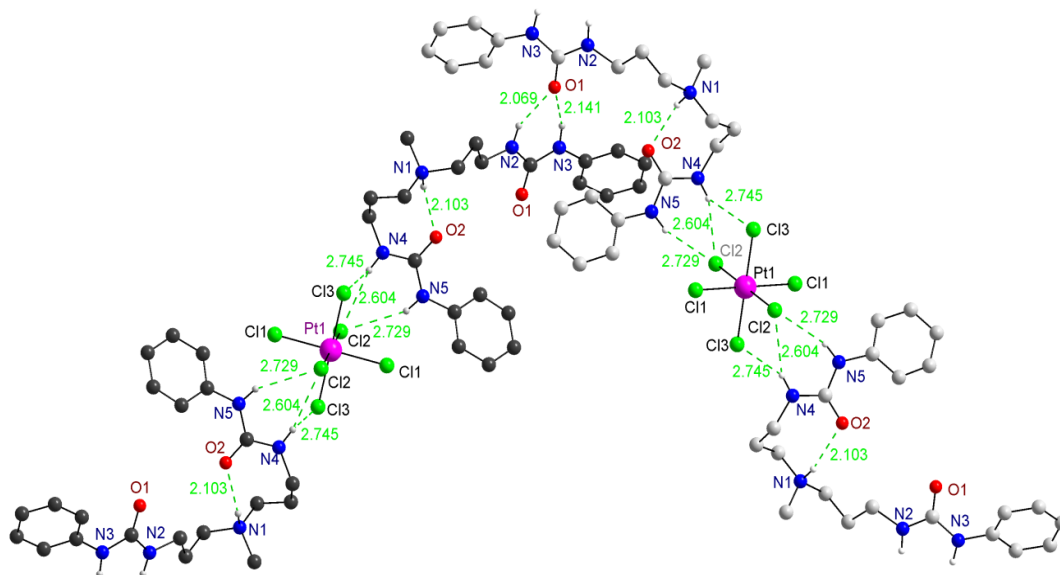
**Scheme 6.** Synthesis<sup>18</sup> of receptors **L**<sup>19</sup>-**L**<sup>24</sup>: a) methyl acrylate, MeOH, RT; b) *n*-hexylamine, 85°C; c) *N*-methylhexylacrylamide, MeOH, reflux; d) methyl acrylate, MeOH, RT; e) *n*-butylamine, 90°C; f) 3-bromopropanoyl chloride, toluene, RT, reflux.



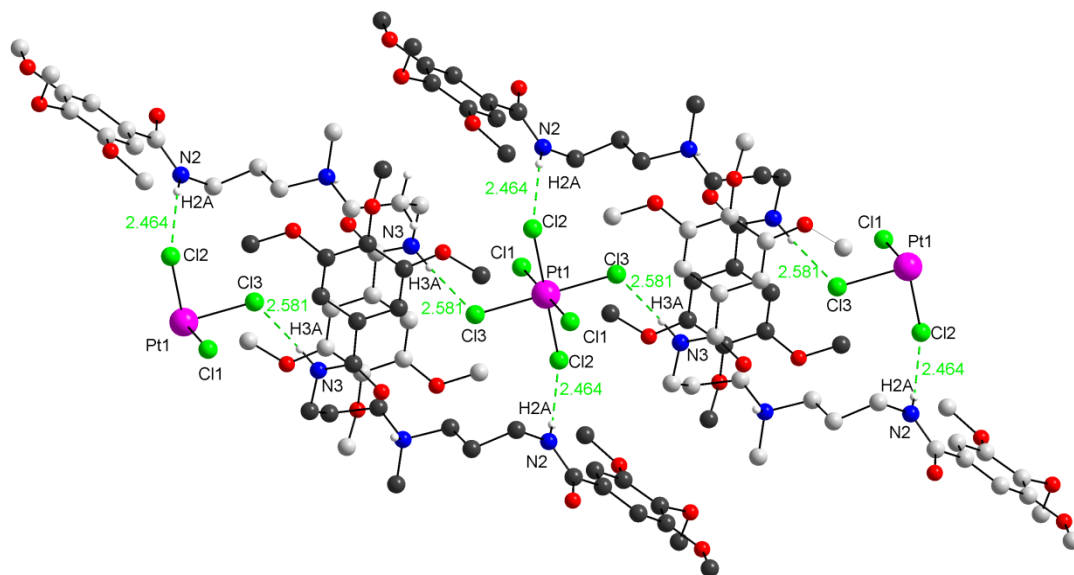
**Figure 1.** Receptors  $L^1$ - $L^5$  previously investigated.<sup>1</sup>



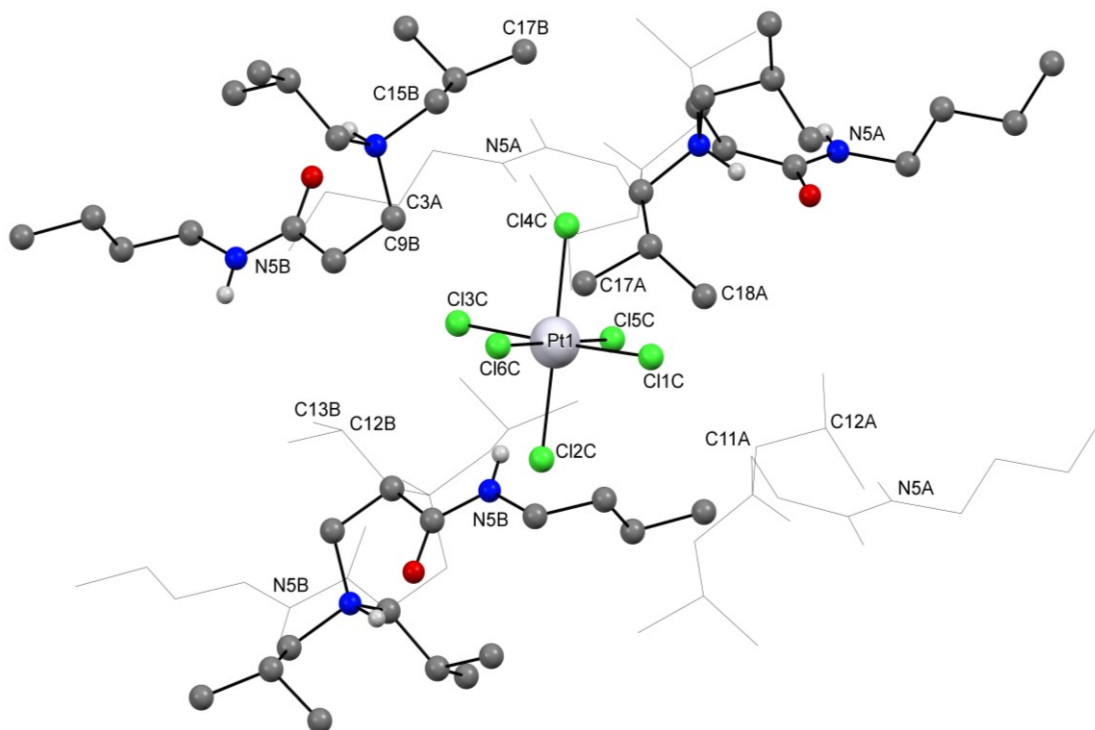
**Figure 2.** Part of the solid state structure of  $L^{11}$  showing the intra- intermolecular hydrogen bonds (H $\cdots$ O distances in Å) formed by one of the two crystallographically independent molecules,  $L^{11(a)}$



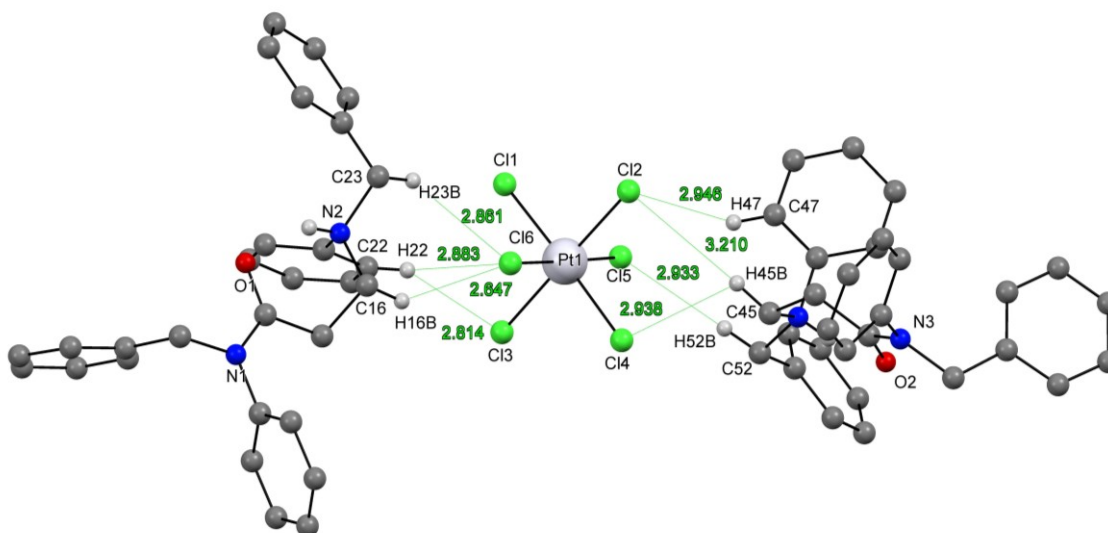
**Figure 3.** The X-ray crystal structure of  $[(L^{11}H)_2PtCl_6]$  showing the shortest  $NH \cdots Cl$  and  $NH \cdots O$  contacts (Å). All hydrogen atoms attached to carbon are omitted for clarity.



**Figure 4.** The X-ray crystal structure of  $[(L^{13}H)_2PtCl_6]$  showing the shortest  $NH \cdots Cl$  and  $NH \cdots O$  contacts (Å). All hydrogen atoms attached to carbon are omitted for clarity.

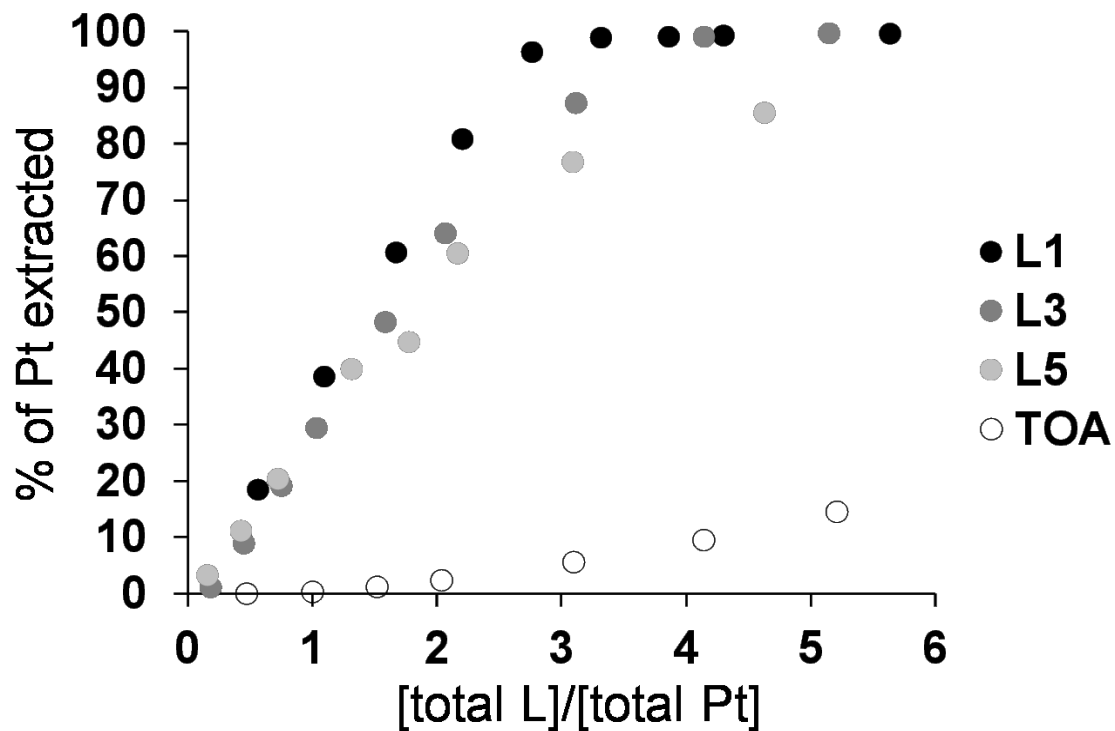


**Figure 5.** The X-ray crystal structure of  $[(L^{23}H)_2PtCl_6]$  showing encapsulation of the  $[PtCl_6]^{2-}$  anion by six protonated receptors. Hydrogen atoms attached to carbon and short contact distances are omitted for clarity.

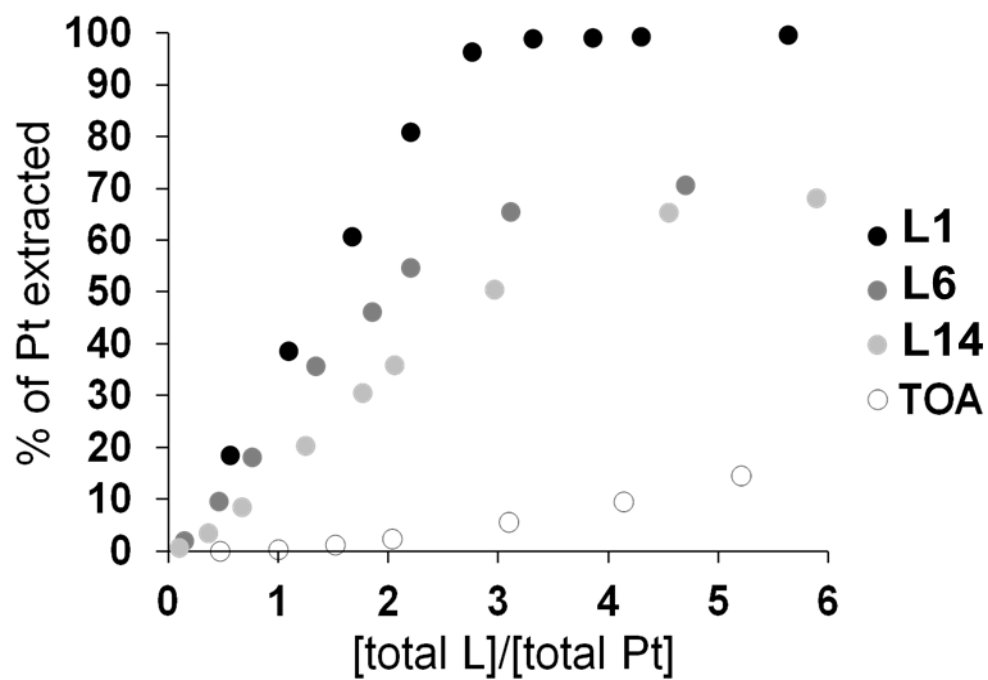


**Figure 6.** The X-ray crystal structure of  $[(L^{24}H)_2PtCl_6]$  showing the shortest  $CH\cdots Cl$  contacts (Å). All remaining hydrogen atoms attached to carbon are omitted for clarity.

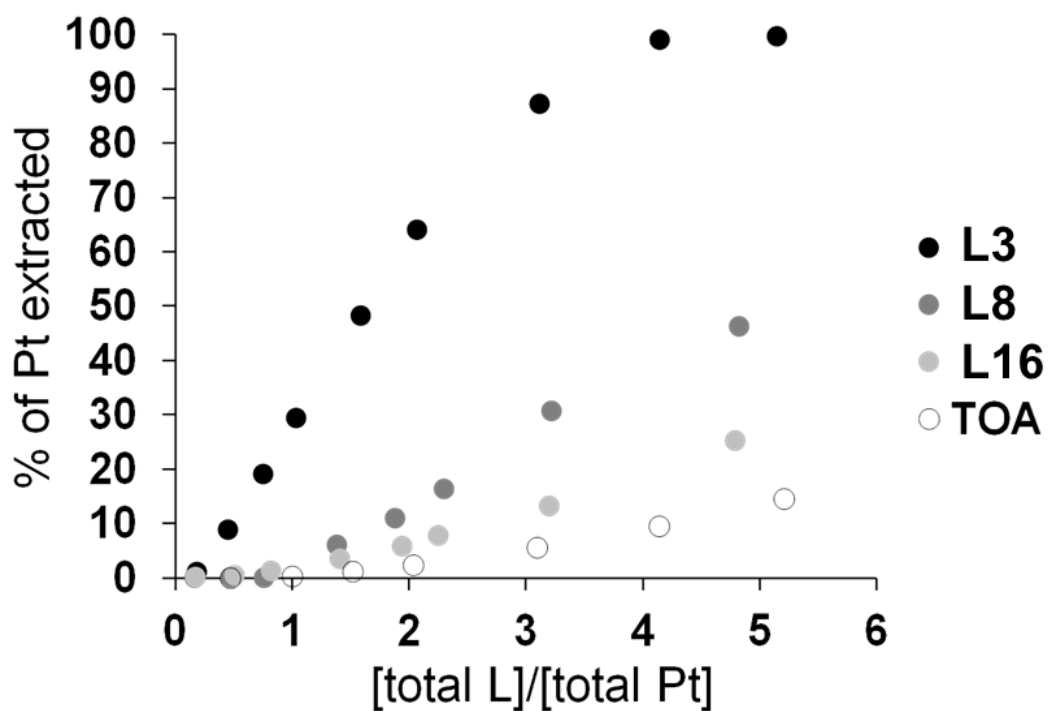




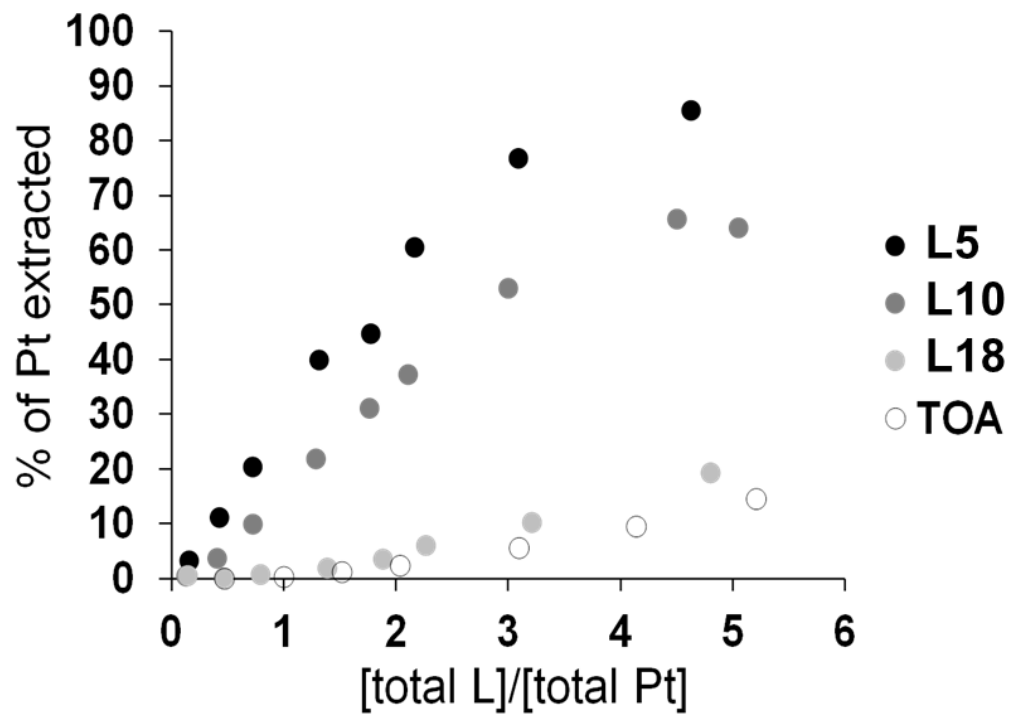
**Figure 7a:** Plot of percentage of the total platinum extracted as  $[\text{PtCl}_6]^{2-}$  from aqueous 0.6 M HCl into  $\text{CHCl}_3$  as a function of the  $[\text{L}]:[\text{Pt}]$  ratio for **L<sup>1</sup>** (tripodal urea), **L<sup>3</sup>** (tripodal amide), **L<sup>5</sup>** (tripodal sulfonamide) and **TOA** for comparison.



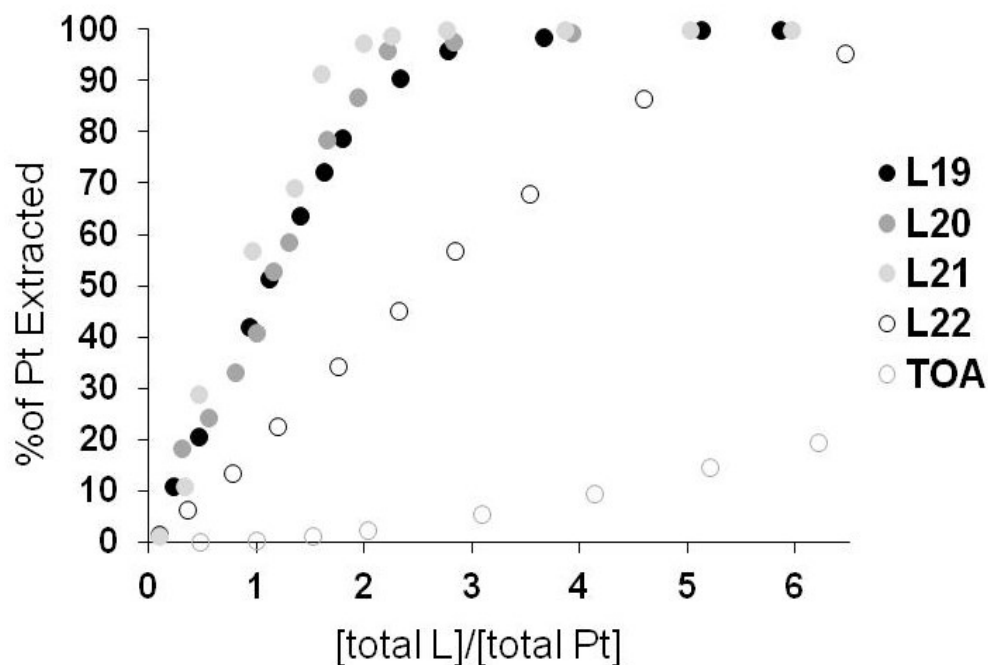
**Figure 7b:** Plot of percentage of the total platinum extracted as  $[\text{PtCl}_6]^{2-}$  from aqueous 0.6 M HCl into  $\text{CHCl}_3$  as a function of the  $[\text{L}]:[\text{Pt}]$  ratio for urea receptors:  $\text{L}^1$  (tripodal),  $\text{L}^6$  (bipodal),  $\text{L}^{14}$  (monopodal), and **TOA** for comparison.



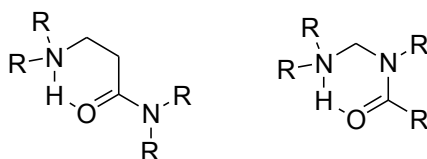
**Figure 7c:** Plot of percentage of the total platinum extracted as  $[\text{PtCl}_6]^{2-}$  from aqueous 0.6 M HCl into  $\text{CHCl}_3$  as a function of the  $[\text{L}]:[\text{Pt}]$  ratio for amide receptors:  $\text{L}^3$  (tripodal),  $\text{L}^8$  (bipodal),  $\text{L}^{16}$  (monopodal), and **TOA** for comparison.



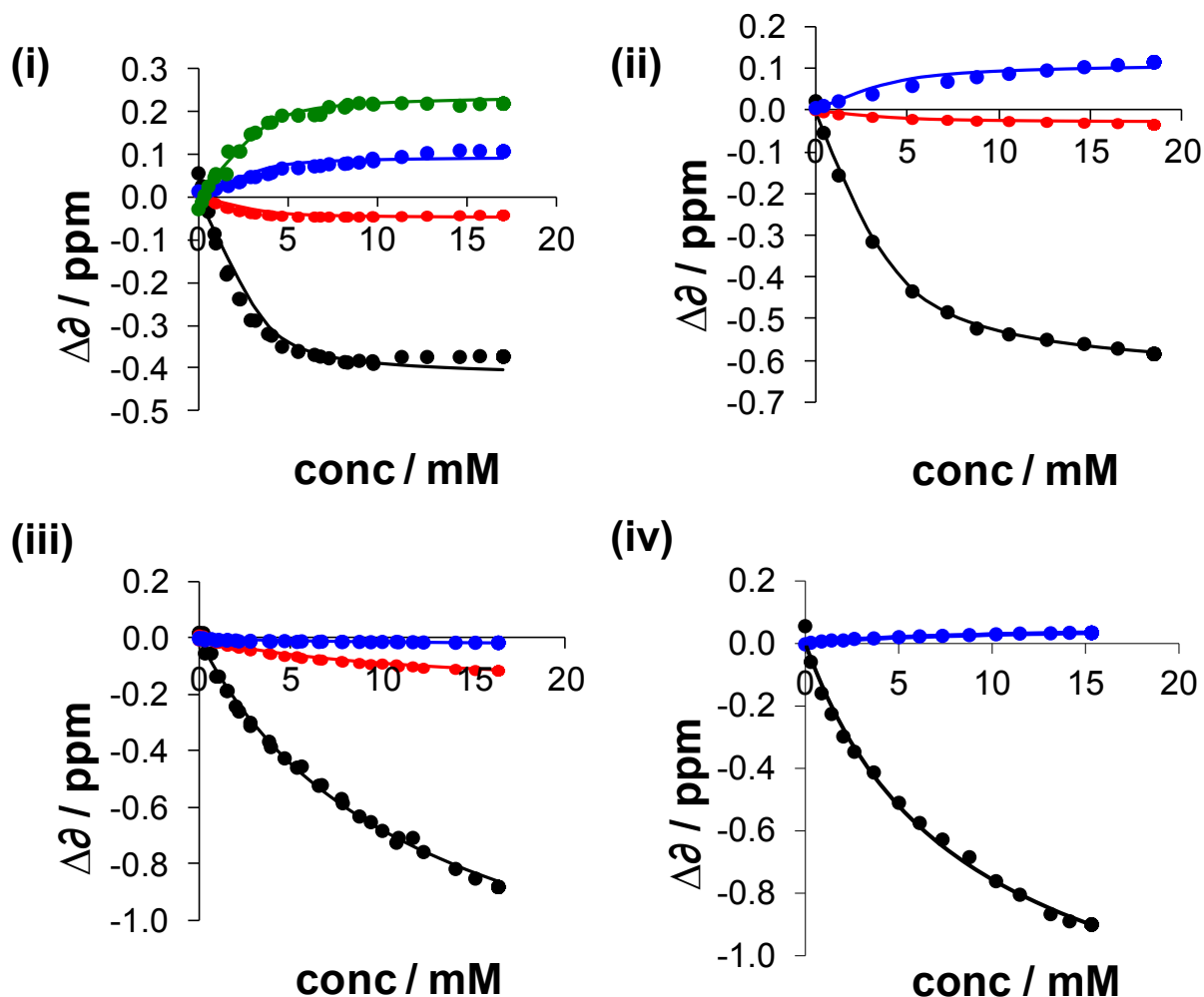
**Figure 7d:** Plot of percentage of the total platinum extracted as  $[\text{PtCl}_6]^{2-}$  from aqueous 0.6 M HCl into  $\text{CHCl}_3$  as a function of the  $[\text{L}]:[\text{Pt}]$  ratio for sulfonamide receptors:  $\text{L}^5$  (tripodal),  $\text{L}^{10}$  (bipodal),  $\text{L}^{18}$  (monopodal), and TOA for comparison.



**Figure 7e:** Plot of percentage of the total platinum extracted as  $[\text{PtCl}_6]^{2-}$  from aqueous 0.6 M HCl into  $\text{CHCl}_3$  as a function of the  $[\text{L}]:[\text{Pt}]$  ratio for the amide receptors: **L**<sup>19</sup>(monopodal), **L**<sup>20</sup> (bipodal), **L**<sup>21</sup> (tripodal), **L**<sup>22</sup> (tertiary amide monopodal) and **TOA** for comparison.



**Figure 8:** The six-membered “proton chelate” rings formed by the receptors **L**<sup>19</sup>-**L**<sup>24</sup> (left) and by a related series of chloridometalate extractants<sup>18,19</sup> (right).



**Figure 9.**  $^1\text{H}$  NMR titrations of  $\text{L}^n\cdot\text{HCl}$  solutions (10 mM in  $\text{CDCl}_3$ ) with  $[(\text{Oct}_4\text{N})_2\text{PtCl}_6]$ : (i)  $\text{L}^4\cdot\text{HCl}$ ; (ii)  $\text{L}^9\cdot\text{HCl}$ ; (iii)  $\text{L}^{17}\cdot\text{HCl}$ ; (iv)  $\text{TOA}\cdot\text{HCl}$ . Signals for the ammonium proton, the *p*-CH, the  $\text{CH}_2$  adjacent to the ammonium nitrogen atom and the  $\text{CH}_2$  adjacent to the amide are shown in black, red, blue and green respectively. The data were fitted (solid lines) to a 2 : 1, host : guest, binding isotherm.

**Table 1** Protonation constants ( $L + H^+ = LH^+$ ) determined in MeCN/H<sub>2</sub>O 50:50 (v/v) (0.1 M NMe<sub>4</sub>Cl, 298.1 ± 0.1 K)

Receptor	pKa
<b>L<sup>1</sup></b>	6.43(7)
<b>L<sup>3</sup></b>	5.94(2)
<b>L<sup>12</sup></b>	8.56(1)
<b>L<sup>13</sup></b>	8.53(1)

\*Values in parentheses are the standard deviations on the last significant figure.

**Table 2.** Percentages of platinum extracted from an aqueous solution of H<sub>2</sub>PtCl<sub>6</sub> (1.1 x 10<sup>-3</sup> M) and HCl (0.6 M) into equal volumes (5 ml) of CHCl<sub>3</sub> solutions of receptors **L<sup>1</sup>** - **L<sup>10</sup>** and **L<sup>12</sup>** – **L<sup>21</sup>** (3.3 x 10<sup>-3</sup> M)

Receptor	% Pt extracted
<b>L<sup>1</sup></b>	98
<b>L<sup>2</sup></b>	98
<b>L<sup>3</sup></b>	87
<b>L<sup>4</sup></b>	86
<b>L<sup>5</sup></b>	77
<b>L<sup>6</sup></b>	65
<b>L<sup>7</sup></b>	62
<b>L<sup>8</sup></b>	30
<b>L<sup>9</sup></b>	25
<b>L<sup>10</sup></b>	53
<b>L<sup>12</sup></b>	28
<b>L<sup>13</sup></b>	13
<b>L<sup>14</sup></b>	50
<b>L<sup>15</sup></b>	51
<b>L<sup>16</sup></b>	13
<b>L<sup>17</sup></b>	9
<b>L<sup>18</sup></b>	10
<b>L<sup>19</sup></b>	97
<b>L<sup>20</sup></b>	98
<b>L<sup>21</sup></b>	100
<b>L<sup>22</sup></b>	40
<b>TOA</b>	5

**Table 3** Association constants ( $K_{\text{ex}}$ ) for the complexation of receptors and the  $[\text{PtCl}_6]^{2-}$  anion (as its tetraoctylammonium salt), as calculated from  $^1\text{H}$  NMR titration experiments at 298 K in  $\text{CDCl}_3$ .

Receptor	No. of amido NH groups	$K$ ( $\text{M}^{-2}$ )
$\text{L}^4\text{H}^+$	3	$6 \times 10^5$
$\text{L}^9\text{H}^+$	2	$1 \times 10^5$
$\text{L}^{17}\text{H}^+$	1	$4 \times 10^3$
$\text{TOAH}^+$	0	$7 \times 10^3$

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## TOC

Modes of attachment of a tripodal extractant to  $\text{PtCl}_6^{2-}$  with pendant amide groups addressing the faces or the edges of the octahedron.

